"On the Ionization of Air for Removal of Noxious Effluvia" (Air Ionization of Indoor Environments for Control of Volatile and Particulate Contaminants With Nonthermal Plasmas Generated by Dielectric-Barrier Discharge)

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Abstract—Recent developments in the application of controllable air ionization processes that apply dielectric-barrier discharge devices to generate nonthermal plasmas have led to applications for chemical and biological decontamination in indoor air environments. These include significant reductions in airborne microbials, neutralization of odors, and reductions of specific volatile organic compounds (VOCs). Removal of very fine particulates (PM_x) is also is enhanced by air ionization. The process of air ionization involves the electronically induced formation of small air ions, including reactive oxygen species, such as superoxide $O_2 \cdot^-$, the diatomic oxygen radical anion, which react rapidly with airborne VOC and PM_x. The physics and chemistry of air ionization, and its utility for contributing to significant improvements in indoor air quality are discussed.

Index Terms—Air ionization, dielectric-barrier discharge, indoor air quality (IAQ), nonthermal plasmas, particulate matter, superoxide, volatile organic compounds (VOCs).

I. INTRODUCTION

AIR IONIZATION: Where We Are Coming From.

"...(A)ir thus loaded with putrid effluvium is exceedingly noxious..."—J. Priestley, "On the Noxious Quality of the Effluvia of Putrid Marshes" (*Phil. Trans.*, vol. 64, pp. 90–95, 1774).

"I have sometimes found the noxious effluvium so very strong ..., that I have hastened out to breathe a purer air."—John Read, "Experiments and Observations Made with the Doubler of Electricity, with a View to Determine Its Real Utility, in the Investigation of the Electricity of Atmospheric Air, in Different Degrees of Purity" (*Phil. Trans. Royal Soc. London*, vol. 84, pp. 266–274, 1794).

Electrical phenomena occurring in ionized gases involve physicochemico-biologically reactive ions, radicals, and molecular species. These phenomena are encountered and overlap among diverse fields of chemistry, physics, engineering, meteorology, climatology, medicine, microbiology, physiology, and industrial hygiene. Each scientific discipline has coined its own "terms of art" for the phenomena: air ionization, corona discharge, nonthermal plasma, dielectric-barrier discharge (DBD), etc. Reports describing gaseous ionization in outdoor ambient (*in ambio*) and indoor (*in camera*) air environments are scattered throughout the literature, both in diverse fields of endeavor and across centuries of time, making evaluations and comparisons challenging. The scientific literature reads across three centuries. The historical quotations cited in this paper are intended to offer appropriate perspectives on this "old-yet-new" technology.

The physical and chemical aspects of small air ions and radicals have been under investigation almost from the discovery of electricity. Plasma chemistry and discharge physics are inexorably intertwined. The health implications of air ionization have been reviewed elsewhere [1]–[7]. Improved diagnostics and mechanistic understandings of electrical discharges in gases [8]–[12] have led to the development of engineered devices with highly controllable processes for the generation of nonthermal plasmas in the treatment of chemical [13]–[19] and biological contaminants [20]–[24]. Coupled with the increased interest in controlling the potpourri of airborne contaminants, there has been an awakening kindled in applying this technology for improving the air quality of enclosed indoor environments [25]–[29]. This paper first provides a background of the physics and chemistry of bipolar air ions. Specific applications of air ionization technology for air cleaning and treatment of indoor air environments is then presented.

II. PHYSICS OF AIR IONS

Air Ionization: What is the Physics?

"It has been ascertained, that the air of most countries, and probably of the whole world, as well as the clouds, fogs, rains, &C. are almost always electrified; but we are ignorant of the office (role) which this electricity can have in the great laboratory of nature; for surely so general and so active a power can hardly be intended by nature, merely to intimidate mankind now and then with thunder and lightning."—Tiberius Cavallo, "Of the Methods of Manifesting the Presence, and Ascertaining the Quality, of Small Quantities of Natural or Artificial Electricity" (*Phil. Trans. Royal Soc. London*, vol. 78, pp. 1–22, 1788).

"In this striking series of phenomena are to be found the essential occurrences of electric arcs, sparks, lightning, aurora borealis and all other phenomena of electric discharge through gases."—Karl T. Compton, "Adventures with Electricity in a Partial Vacuum" (*Scientific Monthly*, vol. 32(1), pp. 69–72, Jan., 1931).

Most matter in the universe is "ionized." In the high vacuum of space, atoms and molecules are present in excited energized states and possess electrical charges. An ionized gas is called a "plasma" [30]. By contrast, most matter on earth (and in the earth's atmosphere) is not ionized. A source of sufficiently high energy is required to induce ionization and separation of charge. Energy can be supplied by natural or artificial (anthropogenic) sources, as derived from nuclear, thermal, electrical, or chemical processes. These sources include: cosmic radiation; ionizing (nuclear) radiation from earth sources, UV light, frictional charging by wind, water-droplet breakup (waterfalls, showers), electrical discharge (lightning), combustion (fire, burning gas jets, engines), and strong electrical fields (corona). Human contributions of air ions include the following:

- combustion processes: simultaneous generation of both ions and particles, the latter also tend to scavenge ions, e.g., smoking, candles;
- indoor environments: synthetic décor and artificial ventilation deplete space charge;
- others: transmission lines produce ion plumes; video displays deplete local charges;
- specific devices: produce air ions for air cleaning or charge neutralization.

Engineered devices for intentional air ionization are more controllable than incidental sources. Recent developments in design and operation of large ion generators have led to commercial availability of energy-efficient units. These units produce controlled outputs of specific ions on demand. The formations of undesirable byproducts, such as ozone, are minimized, and in some applications reduced. Ion generators have been used in a number of applications to control surface static charges. Air ionizers (ion generators) are being used more extensively to clean air in indoor environments.

Ionization is the process, or result of a process, whereby an electrically neutral atom or molecule acquires either a positive or a negative electrical charge. Ionization occurs when energy in excess of the ionization energy is absorbed by an atom yielding a free electron and a positive ion. A free electron can also combine with another atom to form a negative ion. Atmospheric ions have been of scientific interest for more than a century [31]. Observations of chemical actions in electrical discharges in gases go back equally far [32]. The term "air ions" refers broadly to all airborne "particles" that possess electrical charges whose movements are influenced by electric fields [33].

The chemical evolution of air ions, whether created naturally outdoors or artificially indoors depends on the composition of each environment and especially on the types and concentrations of trace species [34]. Specific reactions depend upon the physical properties of individual atoms and molecules, e.g., ionization energy, electron affinity, proton affinity, dipole moment, polarizability, and chemical reactivity. The primary positive ions N_2^+, O_2^+, N^+, and O^+ are very rapidly converted (microseconds) to protonated hydrates, $H^+ \cdot (H_2O)^n (n < 10)$, while the free electrons quickly attach to oxygen to form the superoxide radical anion $^3O_2 \cdot^-$, which also can form hydrates. These intermediate species are collectively called "cluster ions" [35].

Cluster ions react further with trace volatile and particulate constituents. A single cluster ion may collide with as many as $1\,000\,000\,000\,000 (10^{12})$ molecules in air at ground level during its brief ($\sim$ 1 min) lifetime [35]. Subsequent molecular disassociations and reactions in the gas phase and on particulate surfaces complicate reaction schemes in real-world atmospheres. Ion chemistry continually changes through reactions, molecular rearrangements, and growth of molecular ion "clusters" and ionically charged particulates. Protonated hydrates are about one nm (0.001 μm) in diameter with electrical mobilities of 1–2 cm^2/V-s. Ion clusters are about 0.01–0.1 um, with mobilities of 0.3–1×10^{-6} m^2/V-s. The later are larger in size, but orders of magnitude less electronically mobile. Fog droplets or dust particles range up to 10 μm.

Ions and electrons together define overall space charge, i.e., the total free unbalanced charge existing in the atmosphere. Unipolar positive or negative space charge densities can be measured. Fair-weather values for air ions at sea level are $\sim$200–3 000 ions/cm^3 of both polarities. Small ions increase significantly during rainfall and thunderstorms due to natural activation: negative ions may increase to 14 000 ions/cm^3, while positive ions may increase to 7 000 ions/cm^3. The ratio of positive to negative air ions at ground level normally is about 1.1–1.3, decreasing to about 0.9 following certain weather events. Smoking one cigarette can reduce air ions in a room to $\sim$10–100 ions/cm^3.

Small ions and ion clusters have numerous opportunities for collision and reaction with any air impurity. As reactive oxygen species (ROS), they are removed through reaction with other volatile constituents; as reactive charged species (RCS) they are removed through attachment to larger particles by diffusional and field charging. The lifetimes of air ions are strongly dependent on both humidity and temperature, and on the relative concentrations of trace volatile and particulate species. Lifetimes of ions are longer, the lower their concentrations, i.e., less chance of hitting something. Typical lifetime of a naturally generated small air ion in clean air is $\sim$100–1000 s.

III. Chemistry of Air Ions

Air Ionization: What is the Chemistry?

"The influence of physical forces, of modes of aggregation and of mass, not only on the result, but on the manner of the transformation of one kind of matter into another kind—in brief, *the conditions of chemical change*—present a problem to the chemist which only of late years has been submitted to experimental investigation. The difficulties besetting this line of inquiry are many, but the greatest of them is the difficulty of finding a reaction that is simple in kind, that takes place between bodies which can be prepared in great purity, and that yields products which can be exactly measured."—H.B. Dixon, "On Conditions of Chemical Change in Gases" (*Phil. Trans. Royal Soc.*, vol. 175, p. 617, 1884).

Oxygen is required by most lifeforms. There is a dynamic balance, however, between generation of any oxygen species

necessary for life on one hand and protection against its toxic effects on the other [36]–[39]. Four oxidation states of molecular dioxygen are known: $[O_2]^n$, where $n = 0, +1, -1$, and -2, respectively, for dioxygen, dioxygen cation, superoxide anion, and peroxide dianion (symbolically expressed as $^3O_2$, $^3O_2\cdot^+$, $^3O_2\cdot^-$, and $^3O_2^{-2}$. In addition, "common" oxygen in air $^3O_2$ is in a "ground" (not energetically excited) state. It is a free "diradical" having two unpaired electrons. The outermost pair of electrons in oxygen have parallel spins indicating the "triplet" state (the preceding superscript "3," usually omitted for simplicity). Oxygen itself is a common terminal electron acceptor in biochemical processes. It is not particularly reactive, and by itself does not cause much oxidative damage in biological systems. It is a precursor, however, to other oxygen species that can be toxic, including: superoxide anion radical, hydroxyl radical, peroxy radical, alkoxy radical, and hydrogen peroxide. Other highly reactive molecules include atomic oxygen, $O\cdot^-$, singlet oxygen, $^1O_2$, and ozone, O_3. Some of these species are extremely short-lived, while others may persist indefinitely.

Ordinary oxygen does not react well with most molecules, but it can be "activated" by the addition of energy (naturally or artificially derived; electrical, thermal, photochemical, or nuclear), and transformed into ROS. Transformation of neutral oxygen into a reactive state by addition (attachment) of a single electron is called reduction (1). The donor molecule that gave up the electron is oxidized. The result of this monovalent reduction of triplet oxygen is superoxide, $O_2\cdot^-$ It is considered both a radical ($\cdot$, dot sign) and an anion (charge of -1)

$$O_2 + e- \rightarrow O_2\cdot^-. \tag{1}$$

The superoxide radical anion is quantitatively the most important radical formed in humans: a 70-kg adult synthesizes at least 10 kg per year [40]. Approximately 98% of the oxygen consumed by respiring mitochondria is converted to water; the remaining 2% forms superoxide through side reactions in the respiratory chain [41]. Human cells constantly produce superoxide (and the reactive molecules derived from it) as an "antibiotic" against invading micro-organisms. The biology of small air ions [1]–[3] and oxygen radicals [36]–[39] has been reviewed. Superoxide, along with nitric monoxide radical, $NO\cdot$, acts as signaling molecules to regulate many cellular processes. Under biological conditions, as described in a vast literature, it reacts with itself to produce hydrogen peroxide and oxygen through a reaction (2) known as "dismutation", which can be spontaneous, or catalyzed by superoxide dismutase ("SOD")

$$2O_2\cdot^- + 2H^+ \rightarrow H_2O_2 + O_2. \tag{2}$$
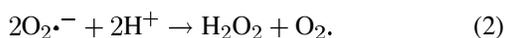
Superoxide is both an oxidant (electron acceptor) and a reductant (electron donor). It is involved in production of the highly reactive hydroxyl radical (HO$\cdot$), catalyzed by metallic ions and sunlight. Superoxide reacts with nitric monoxide radical (NO$\cdot$) *in vivo* to produce peroxynitrate (OONO$\cdot$), another highly reactive oxidizing molecule. Superoxide undergoes further reduction to peroxide (O_2^{-2}), an activated form of oxygen, usually known as "hydrogen peroxide" (H_2O_2), in aqueous systems, necessary for health.

Superoxide is the dissociated form of a weak acid, the hydroperoxyl radical, $HO_2\cdot$. In aqueous systems, the relative proportions of these two species depend upon pH, and the appropriate equilibrium constant. Superoxide also is formed in air as a negative ion [42]. The generation of low concentrations of hydrogen peroxide in wet air subjected to negative air ionization also has been confirmed [38], [43], [44].

In the absence of metallic impurities, a solution of superoxide in strong alkali can be kept in the refrigerator overnight. By contrast, superoxide ion clusters formed in air react rapidly with airborne particulates and volatile organic species. While hydrogen peroxide is an oxidizing agent, the combination of hydrogen peroxide and superoxide (3) yields a much more reactive species, the hydroxyl radical, HO$\cdot$, one of the strongest known oxidants

$$O_2\cdot^- + H_2O_2 \rightarrow O_2 + HO\cdot + HO^-. \tag{3}$$

Identification of individual chemical species that might become involved in chemical reactions in air environments is not trivial. Modeling of the reaction scheme may involve dozens of homogeneous and heterogeneous reactions among the aforementioned species. The formation of transient intermediates adds complexity.

IV. REACTIVE OXYGEN SPECIES/REACTIVE CHARGED SPECIES

Air Ionization: A Chemical Perspective.

"In the case of gases, it has been known, since the time of Priestley and Cavendish, that the spark discharge has the apparently antagonistic properties of causing decomposition in some cases and combination in others."- Thomas Andrews and Peter G. Tait, "On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and Other Gases" (*Phil. Trans. Roy. Soc. London*, vol. 150, pp. 113–131, 1860).

"From a chemical perspective, the indoor environment is a reaction vessel with chemicals continually entering and exiting. Some of these chemicals can react with one another (or themselves) creating reaction products that might otherwise be absent from the indoor setting."—C. J. Weschler and H. C. Shields, "Potential Reactions Among Indoor Pollutants" (*Atm. Environ.*, vol. 31(21), pp. 3487–3495, 1997).

Oxygen, superoxide, peroxide, and hydroxyl species are all ROS that participate in a potpourri of oxidation-reduction reactions in solid, liquid, and gaseous phases [28], [45], [46]. Concerns for limiting excessive levels of ROS *in vivo* to reduce adverse health effects are tempered by other concerns for increasing their levels *in enviro* to reduce adverse environmental effects. ROS are significant in the atmospheric destruction of organics, but they also participate in the ground-level formation of "smog" and the tropospheric destruction of ozone (O_3). The hydroxyl radical is key to the tropospheric destruction of volatile organic compounds through a series of complex chemical reactions involving oxidation (abstracting electrons from organic compounds), which in turn can react with other organic molecules in a chain reaction.

The chemistries of ROS in the form of ions are encountered from "inner" to "outer" space. Solid-state sensors of the SnO$_2$ type, commonly used to "sense" trace gases, are affected by

chemisorption of oxygen and water vapor. At sufficiently high operating temperature, O_2 from air is adsorbed onto crystalline surfaces having negative charges. Donor electrons in the crystals are then transferred to the adsorbed O_2 forming superoxide radicals that react with CO, hydrocarbons, and other trace gases or vapors. The resulting liberation of electrons decreases the surface charge and produces an increase in conductance that is then "sensed." Similar chemistries are encountered in photocatalytic oxidation processes [47], [48], solid-oxide fuel cells, and various nonthermal plasma processes. Chemicalionization, nuclearionization, photoionization, and electroionization techniques are used in analytical chemistry to separate and to identify chemical spectra. Chemical-ionization mass spectroscopy (CIMS) is an important tool of analytical chemistry in which "reagent" ions are electronically generated to react at very low levels with "target" molecules in very specific reactions [49]. Matrix-assisted laser desorption ionization (MALDI) is another analytical technique that involves a laser ablation technique to fragment biological molecules.

Space scientists have postulated that the unusual reactivity of the Martian soil and the absence of organic compounds are explained by ultraviolet radiation which causes oxidation of metal atoms and the creation of ROS on the soil grains [50]. The three radical ROS most commonly formed in nonthermal plasmas from dioxygen O_2 are: $O{\cdot}^-$, $O_2{\cdot}^-$, and $O_3{\cdot}^-$. [51], [52]. Of these, $O_2{\cdot}^-$ is the least reactive, the most stable, and the most likely oxygen radical species to be encountered at ambient temperatures on earth. Its chemistry involves reaction with water to form hydrated cluster ions [53]. Two associated species, hydroperoxide and hydroxide, are capable of oxidizing organic molecules. Superoxide reacts with water (4) to produce oxygen, and perhydroxyl and hydroxyl radicals, which also can oxidize organic molecules

$$2O_2{\cdot}^- + 2H_2O \rightarrow O_2 + HO_2{\cdot}^- + HO^{\cdot}. \tag{4}$$
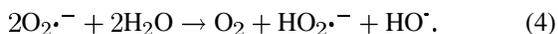
Superoxide may also react directly with ozone to form hydroxyl anion and hydroxyl radical (5). This is postulated as a route for O_3 removal

$$2O_2{\cdot}^- + O_3 + H_2O \rightarrow 2O_2 + HO^- + HO^{\cdot}. \tag{5}$$
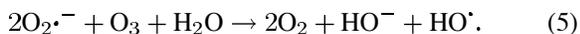
A reaction scheme (6) might be postulated in which superoxide, and other ROS generated by air ionization, depicted simply as O_2, initiate the oxidation of volatile organic compounds, and also semivolatile organic compounds associated with airborne particulates

$$C_xH_y + (x + y/4)O_2 \rightarrow xCO_2 + (y/2)H_2O. \tag{6}$$

This simplistic representation is patterned after the calculation of the theoretical oxygen demand (ThOD) for wastewater treatment and the calculation of the oxygen required for thermal combustion. A more generalized "reaction" of volatile organic compounds (VOCs) with ROS and particulate matter (PM_x) with RCS might be invoked to yield terminal oxidation products from the organics and a larger size distribution of the particulates that are more easily removed or tolerated

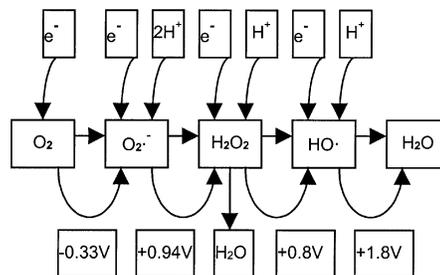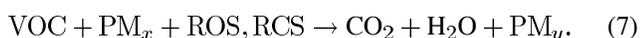$$VOC + PM_x + ROS, RCS \rightarrow CO_2 + H_2O + PM_y. \tag{7}$$

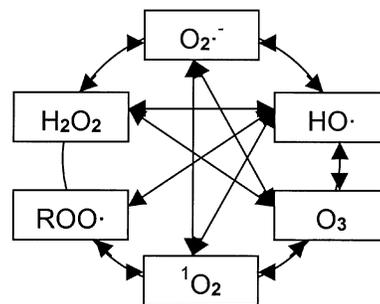Fig. 1.   Sequential reduction of the oxygen molecule.

Fig. 2.   Interconversion of oxygen species.

Many reaction schemes have been suggested, depending on whether focus was placed upon detection of stable reaction products or the more difficult detection of transient intermediates [54]–[56]. These generally involve excitation, dissociation, ionization, and electron-capture reactions. For any given ROS, there exists some confirmed or postulated reaction scheme for interconversion to any of the other species. This may take the form of a series of sequential reductions (electron transfers) beginning with the dioxygen molecule and ending with the water molecule [39] (Fig. 1).

Alternatively, the interconversion of ROS can be depicted in a cyclic pattern [39] (Fig. 2). Similar transformations occur in the natural environment. The key to effective air ionization is twofold: i) maximize the formation of those ROS that beneficially react to form desirable end products like carbon dioxide and water and ii) minimize the formation of other ROS that adversely react to form undesirable intermediate products.

Speciation of VOCs during air ionization, i.e., the disappearance of parent species and the formation of byproducts, other than carbon dioxide and water, has been speculated upon and modeled [57]–[60]. The impact of electron-driven chemistry was the subject of a recent workshop [61]. It was stated to be "well-known" that nonthermal, gas-phase plasmas that are electronically generated at ambient temperature and atmospheric pressure can destroy low initial concentrations of VOCs. Ionization was particularly applicable to treating air containing relatively low initial concentrations of ten common VOCs using a packed-bed, pulse-corona reactor [62]. Destruction efficiencies were estimated by comparing ionization energies.

The ionization energy (IE) is the amount of energy, expressed in units of electron volts (eV), required to effect the removal of an electron from a molecule or atom leading to the formation of an ion.). IE values are available for a number of chemicals [63] reported by a number of private and governmental researchers

TABLE I
CHEMICAL COMPOUNDS AMENABLE TO
TREATMENT BY AIR IONIZATION

	Chemical	Formula	IE, eV
1.	Phenanthrene	$C_{14}H_{10}$	7.89
2.	Pinene, α-	C_8H_{19}	8.07
3.	Naphthalene	$C_{10}H_8$	8.14
4.	Trimethylbenzene, 1,2,4-	C_9H_{12}	8.27
5.	Limonene (1-Pentene)	$C_{10}H_{16}$	8.3
6.	Xylene, p-	C_8H_{10}	8.44
7.	Styrene	C_8H_8	8.46
8.	Xylene, o-, m-	C_8H_{10}	8.55
9.	Ethyl Benzene	C_8H_{10}	8.77
10.	Toluene	C_7H_8	8.83
11.	Cyclohexene	C_6H_{10}	8.95
12.	Chlorobenzene	C_6H_5Cl	9.07
13.	Benzene	C_6H_6	9.24
14.	Nitric Oxide	NO	9.26
15.	Tetrachloroethylene	C_2Cl_4	9.33
16.	Trichloroethylene	C_2HCl_3	9.46
17.	Methyl Ethyl Ketone	C_3H_8O	9.52
18.	Nitrogen Dioxide	NO_2	9.59
19.	Dichloroethylene, trans-1,2-	$C_2H_2Cl_2$	9.64
20.	Octane	C_8H_{18}	9.80
21.	Cyclohexane	C_6H_{12}	9.88
22.	Butyl Acetate, n-	$C_6H_{12}O_2$	9.92
23.	Heptane, n-	C_7H_{16}	9.93
24.	Ammonia	NH_3	10.07
25.	Hexane, n-	C_6H_{14}	10.13
26.	Acetaldehyde	CH_3CHO	10.23
27.	Methyl Acetate	$C_3H_6O_2$	10.25
28.	Pentane, n-	C_5H_{12}	10.28
29.	Hydrogen Sulfide	H_2S	10.46
30.	Ethyl Alcohol	C_2H_5OH	10.48
31.	Ethylene	C_2H_4	10.51
32.	Butane	C_4H_{10}	10.53
33.	Methyl Alcohol	CH_4O	10.84
34.	Formaldehyde	CH_2O	10.88
35.	Trichloroethane, 1,1,1-	$C_2H_3Cl_3$	11.0
36.	Trichloroethane, 1,1,2-	$C_2H_3Cl_3$	11.0
37.	Carbonyl Sulfide	COS	11.18
38.	Phosgene	$COCl_2$	11.2
39.	Halon FC 12-B	$CClBrF_2$	11.21
40.	Methyl Chloride	CH_3Cl	11.26
41.	Methylene Chloride	CH_2Cl_2	11.33
42.	Tetrachloromethane	CCl_4	11.47
43.	Ethane	C_2H_6	11.52
44.	Nitric Acid	HNO_3	11.95
45.	CFC-113	$C_2Cl_3F_3$	11.99
46.	CFC-12	CCl_2F_2	12.0
47.	Oxygen	O_2	12.07
48.	Methyl Cyanide	C_2H_3N	12.20
49.	Sulfur Dioxide	O_2S	12.35
50.	Sulfuric Acid	H_2O_4S	12.40
51.	Ozone	O_3	12.53
52.	Methane	CH_4	12.61
53.	Water	H_2O	12.62
54.	Hydrogen Chloride	HCl	12.74
55.	Nitrous Oxide	N_2O	12.89
56.	Hexafluoroethane	C_2F_6	13.6
57.	Hydrogen Cyanide	HCN	13.60
58.	Carbon Dioxide	CO_2	13.78
59.	Carbon Monoxide	CO	14.01
60.	Nitrogen	N_2	15.58

in the open literature to be chemically altered or destroyed by air ionization or allied processes (Table I). As a first estimation, those chemicals with lowest IE are most amenable to treatment by air ionization. Those with IE > oxygen are most difficult. Because ionization energies and bond dissociation energies may be of comparable magnitudes (<10 eV), kinetics govern which reactions predominate. Specific energy consumption (eV/molecule) (or its reciprocal, the G-value) can be used to determine relative ion efficiency [64]. Treatment efficiencies vary with

temperature, relative humidity, and oxygen content, but are surprising independent of concentration, power, and airflow.

Air ionization involves reactions of electrically charged species: 1) recombination with other air ions; 2) reaction with gaseous molecules; 3) attachment to larger particles; and 4) contact with surfaces. The former two processes generally involve ROS in the removal of volatile organic compounds; the latter two processes generally involve RCS in the removal of particulate matter. The former includes bipolar ions, free radicals, and radical ions; the latter includes cluster ions, hydrated ions, and charged particles.

V. AIR-CLEANING TECHNOLOGIES

Air Ionization: Let us Clear the Air!

"Although the electrical discharge in gases has been investigated in its various phases ever since the study of electricity itself began, it is only in the last five or six years that our knowledge of the subject has begun to take systematic and satisfactory form."—Earnest Merritt, On reviewing the new book by J. J. Thomson (Lord Kelvin), "The Discharge of Electricity Through Gases" (Charles Scribner's Sons, New York: 1899; *Science*, vol. 9, pp. 289–291, 1899).

Air-cleaning technologies have been cataloged [25], [65]–[67] by functionality and specificity for removal and/or destruction of PM_x and/or VOCs. They include: 1) physical; 2) physicochemical; and 3) electronic processes, and various combinations. Air-cleaning processes fall into one or more of six overlapping classifications (Table II). Solid media filtration of PM_x involves physical or mechanical collection of particles on porous granular or fibrous media. Mechanisms of removal are impaction, settling, and diffusion. Gas-phase "filtration" involves sorption of VOCs onto surfaces, and into pores of solid media, with or without chemical reactions. Catalytic oxidation includes solid media with imbedded catalysts or photochemically active materials.

Electronic air-cleaning systems are cataloged by types of ionization and modes of operation [68], [69]. They include: bipolar air ionization, ozone generation, and electrostatic precipitation. Air ionization forms "nonthermal" plasmas, i.e., the electron and ion clusters are highly but uniformly energized (heated). The bulk of the surrounding neutral gases, however, remains at ambient temperature. Thermally speaking, the mixture is in "nonequilibrium." Air ionizers produce local clusters of bipolar (±) ions. Clustered ions then electrically charge PM_x thereby facilitating their removal by filtration. Cluster ions also chemically react and destroy VOCs. This process, although similar to many familiar oxidation processes, is more subtle and complex. It is effected at ambient temperature without the need for solid catalysts. Microbials are inactivated, destroyed, and/or agglomerated by bipolar ions.

It is important to distinguish the various types of electronic air cleaners [65], [66], [70]. Air ionizers are distinct from both electrostatic precipitators and ozone generators. In air ionization, PM_x is electrically charged through direct contact with bipolar air ions, vis-à-vis attraction of particles to electrically charged surfaces in the case of electrostatic precipitation. In air ionization, the primary active species are ROS other than ozone,

TABLE II
COMPARISON OF AIR-CLEANING SYSTEMS

Technology	Bipolar Air Ionization	Ozone Generation	Electrostatic Precipitation	Gas-Phase Filtration	Solid Media Filtration	Catalytic Oxidation
Function	Electronic	Electronic	Electronic	Physicochemical	Physical	Physicochemical
Principle	DBD (Dielectric Barrier Discharge).	Sparking Discharge.	High-voltage wire and plate.	Sorption and reaction.	Flat, pleated, or HEPA media.	Solid catalysts with or without UV.
Process	(+) & (-) Ion generation.	Ozone generation.	Charging of particulate matter.	Sorption and reaction.	Collection on porous media.	Catalytic oxidation.
Active Species	Reactive Oxygen & Charged Species.	Ozone (O_3).	Charged particles.	Sorption and reaction sites.	High surface area.	Reactive oxygen species.
Products	CO_2, H_2O, larger PM_x	CO_2, H_2O, O_3	Larger PM_x	Less VOCs	Less PM_x	Less VOCs
Byproducts	Min. byproducts, O_3 is controlled.	Significant O_3, atm. reactants.	O_3, if not cleaned regularly.	Spent media with contaminants.	Spent filters; contaminants.	Exhausted or fouled catalysts
Health Concerns	O_3, limited by control.	High ozone exposure.	Exposure to high voltages and O_3.	Breakthrough, spent media disposal.	Contaminated filter disposal.	Catalyst disposal or recovery.
VOCs	Chemical oxidation	Chemical oxidation	Sorption of VOCs on PM_x	Ad/absorption	NA	Chemical oxidation
PM_x	Agglomeration.	Not applicable	Collection on plates.	Collection in media.	Impact, settling, and diffusion.	NA
Microbials	Inactivation, destruction, agglomeration.	Inactivation.	Particle removal.	NA	Particle removal.	Inactivation
Control	Ions on demand.	Continuous generation.	Process design.	Process design.	Process design.	Process design

vis-à-vis nascent ozone in the case of ozone generation. Valid issues have been raised on ozone toxicity [71], [72], the utility of ozone generators [73]–[76], and secondary reactions of ozone with specific classes of indoor pollutants [77]–[79]. There are similarities in the physical phenomena occurring with ozone generators and air ionizers, but there are major differences in design and operation. Conditions optimal for air ionization are not optimal for ozone generation. The presence of water vapor promotes HO·, reduces ozone, and increases oxidation of organics [80], [81].

VI. OPERATION OF AIR IONIZERS

Air Ionization: How is It Done?

"It will be readily allowed, that an apparatus capable of rendering perceptible, or, as it were, of magnifying the smallest, and otherwise unobservable, degrees of natural as well as artificial electricity, is of great advantage to the science of electricity in general, and especially for the investigation of atmospheric electricity."—Alexander Volta, "Of the Method of Rendering Very Sensible the Weakest Natural or Artificial Electricity" (*Phil. Trans. Royal Soc. London*, vol. 72, p. 237, 1782).

"The great importance of a machine for the purpose of detecting very minute quantities of electricity has occurred to many of the cultivators of this science; as by such an assistant not only many chemical combinations or solutions, but also many yet unexplained atmospheric phenomena, may become intelligible."—Abraham Bennet, "An Account of a Doubler of Electricity" (*Phil. Trans. Royal Soc. London*, vol. 77, pp. 288–296, 1787).

"Before proceeding further, we must draw attention to the difference of action which, in many cases, we have found to exist between the spark, or spark discharge, and the glow, or silent discharge."—Thomas Andrews and Peter G. Tait, "On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and Other Gases" (*Phil. Trans. Roy. Soc. London*, vol. 150, pp. 113–131, 1860).

Air ionizers create charged air molecules upon the application of an energy source. By energetically either adding or removing an electron, air molecules are given a negative or positive charge (usually oxygen or nitrogen species, respectively). Three modes of ionization have been employed: photon ionization, nuclear ionization, and electronic ionization. Photon ionization uses a low-energy X-ray energy source to displace electrons from the gas molecules. Nuclear ionizers use polonium-210 radiation sources that emit alpha particles which then collide with the gas molecules and displace electrons. Molecules that lose electrons become positive ions. Neutral gas molecules rapidly capture these free electrons and become negative ions. These types of ion generators do not have electrodes, so deposits are not a concern. X-ray and nuclear sources must be carefully installed and controlled to avoid creating safety hazards.

Electronic ionizers, or corona-discharge ionizers, are devices that historically contained electrodes configured either as sharp emitter points or as flat wires. Strong electric fields interacting with electrons of adjacent gas molecules produce ions of the same polarity as the applied voltage [8]. Electrode configuration is especially important in defining the character of the corona and the propensity to produce or not produce ozone [82]. Ionizers are classified according to the type of electrical current that is applied to the emitter electrodes: pulsed or steady-state dc or ac. AC devices are "bipolar" ionizers in that they alternately produce clouds of both negative and positive ions within each current cycle.

Electrical discharge devices incorporating dielectric barriers placed between electrodes have been configured as cylinders, flat plates, and packed beds of granular dielectric or ferroelectric media. The general process is known as DBD and is an inherently complex stochastic process [83]–[86]. The development of such DBD devices have been reviewed [14], [24]. Industrial
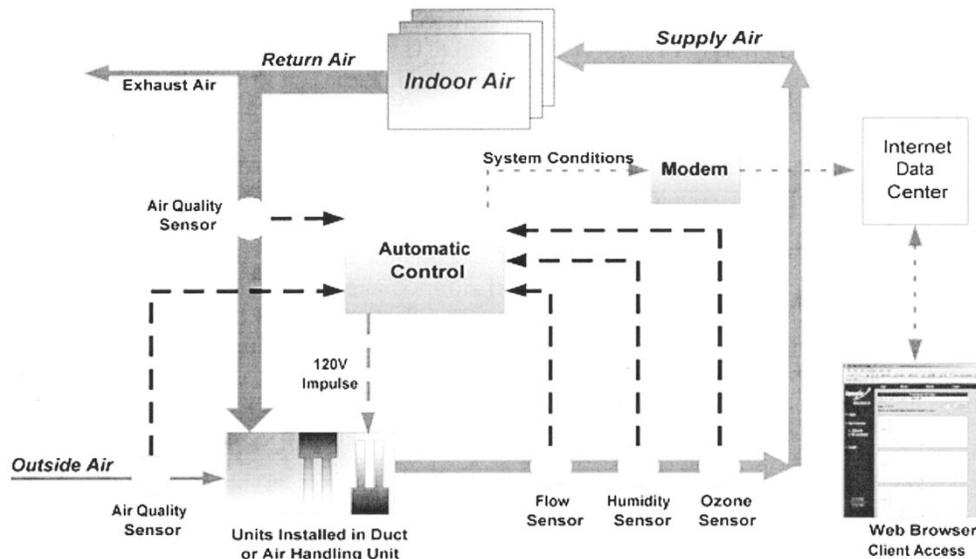
Fig. 3.   Air ionization: process schematic.

applications include: traditional ozone generation, surface treatment of polymer films, microchip etching, pollution control, excimer lamps and plasma displays, and carbon-dioxide lasers. One particularly useful configuration is a cylindrical glass tube placed between a coaxial outer electrode and a wire inner electrode. Glass, being a dielectric material, acts as a barrier to the applied electric field. In most gases at atmospheric pressure, electrical breakdown occurs in the form of microdischarges that are filamentary and diffuse, i.e., many small discharges of very short duration, rather than a few large discharges [87], [88]. Process control of microdischarges is important in optimization [89], [90].

In addition to electrode configuration and type of current, formations of clustered ions and other transient chemical species are affected by the relative concentrations of positive and negative ions, reactive target species (either volatile of particulate), and relative humidity. AC ionizers have inherent voltage swings as the electric fields being produced move from positive to negative maxima. Such swings may cause more intense corona discharges that in turn can produce undesired byproducts unless controlled. DBD devices which produce multiple "microdischarges" (i.e., a multitude of current filaments of short duration) have been developed that allow for improved process control and reduced formation of undesirable species such as ozone.

Air ion generation is measured with charged-plate monitors, as defined in the ESD Association Ionization Standard ANSI EOS/ESD S3.1-1991. An alternative device uses an electrostatic-field meter to measure static decay on glass substrates. One example (Ionmeter T-111, Transjonic AB, Kållered, Sweden) is a Langmuir-type device with resolution of ± 20 ions/cm^3. Another example is a less expensive device (Air Ion Counter, AlphaLab, Salt Lake City, UT) is sensitive down to 10 ions/cm^3 with a range of 10–1 999 999 ions/cm^3. Direct monitoring of ions (or indirect monitoring of air contaminants) allows for generation on demand of sufficient ions of appropriate charge.

A typical building HVAC system involves conditioning of makeup outside air in an air-handling unit (AHU), transport of supply air to building spaces, and transport of return air back to the AHU, with discharge of exhaust air. A typical air ionization system with automatic controls is designed for flexible installation, operation, and data acquisition (Fig. 3). air ionization process controls have multiple options: sensors for monitoring air quality (VOCs and PM$_x$), electronic monitoring of air ions, and ionization modules to generate ions on demand. The design of the system is dependent upon the application (home, office, laboratory, public building, commercial establishment, etc.), the nature of the IAQ problem to be controlled, and the level of performance to be achieved.

Locations of air ionization units are tailored to particular residential, commercial, industrial, or public facilities depending upon sources and strengths of VOCs and PM$_x$. Air ionization modules are fitted directly into the central AHU to treat the entire airflow. Alternatively, the modules can be fitted into the existing ductwork downstream of the central HVAC system. Freestanding devices can also be located in individual room spaces to meet immediate demands.

Proper operation of an air ionization system to improve indoor air quality requires optimization of up to eight process variables describing both the physical air handling system and the demand. A process control unit is centrally located. Inputs are set manually, based on fixed situation design parameters, and automatically, based on monitored demand parameters. Three manual inputs include: desired ion intensity level, power capacity, and airflow area. Five electronic inputs include: airflow, humidity, outside air quality, return air quality, and ozone detection. A flow sensor measures volumetric airflow (cfm), and a humidity sensor measures airborne water vapor. Air quality sensor(s) determine the relative demand for air ionization. Air quality sensors can be placed both in the return air duct and in the outside air intake. Metal oxide sensors (MOSs) can be used to measure total volatile organic compounds (TVOCs). Another air quality sensor can be used to monitor ozone, to insure that

TABLE III
CASE HISTORIES FOR AIR IONIZATION

Case History	Location	Application Objectives				
		VOCs	PM$_x$	Odors	Smoke	Microbes
Engineering Center	Major city	X				
Travel Center	International airport	X	X			
Vintage Hotel	City center			X		
Modern Hotel	International airport	X	X			
Shopping Center	Metropolitan center	X				
Parliament Building	Capital city	X		X		X
Restaurant Complex	Central plaza			X		
Individual Restaurant	City center			X	X	
Meat Processing	Odor from waste					X
Meat/Food Storage	Supermarket			X		X
Anatomy Laboratory	Medical school	X				
Pathology Laboratory	Hospital					X
Soccer Stadium	Major city			X		
Furniture Plant	Manufacturing site				X	
Printing Plant	Small city	X				
Hairdresser	Nail polishing	X				
Research Laboratory	Animal Handling			X		X
Gaming/Smoke Shop	Indian Reservation					

TABLE IV
CASE HISTORY A: ENGINEERING CENTER

Component Classes (Number)	Without Ionization, µg/m^3	With Ionization, µg/m^3
Aromatics (13)	70	37
Alkanes (9)	5 – 1	4 - < 1
Iso-Alkanes (3)	4 - < 1	1 - < 1
Cyclo-Alkanes (3)	8 – 1	4 - < 1
Alcohols (8)	< 10	< 10
Ketones (7)	< 10	< 10
Esters (3)	< 10	< 10
Chlorinated Hydrocarbons (9)	2 - < 1	2 - < 1
Terpenes (5)	3 - < 1	1 - < 1
Total VOCs (59)	112	56

any ozone present in the outside air or incidentally formed at low levels, is below recommended the ASHRAE limit (50 ppb). A third type of air quality sensor can be used to measure relative levels of certain size fractions of particulate matter (PM$_x$). Signals from the sensors can be logged by a personal computer or transmitted by modem to an internet data center. Performance of the system can be visually displayed on a series of real-time plots and stored for archival retrieval or real-time viewing using a standard web browser.

VII. APPLICATIONS

Air Ionization: Zapping the Stuff in Air.

"The molecular changes produced by the electric current, or discharge, in certain compound bodies through which it is transmitted, furnish some of the most interesting examples of the action of a decomposing force that have been discovered in later times."—Thomas Andrews and Peter G. Tait, "On the Volumetric Relations of Ozone, and the Action of the Electrical Discharge on Oxygen and Other Gases" (*Phil. Trans. Roy. Soc. London*, vol. 150, pp. 113–131, 1860).

Air ionization has a long history in varied applications. Air ionization is applied for air cleaning where increasingly more stringent controls are demanded. volatile organic compounds (VOCs), e.g., odors, are oxidized by ROS. PM$_x$, e.g., environmental tobacco smoke (ETS), pollen, and dust, are agglomerated by RCS). Microbials are inactivated, destroyed, and/or agglomerated. Less energy is required since less outside makeup air is used. Typical air ionization systems have been installed in domestic and office locations, as well as in institutional, commercial, and industrial locations (Table III).

One such air ionization system was installed in a large engineering center (Siemens AG, Berlin, Germany) with several hundred workers in a multifloor office facility. Reductions in 59 specific VOCs representing nine classes of VOCs were quantitated (Table IV). Specific VOCs were analyzed by GC/MS from samples collected on sorbent tubes during representative periods of operation with and without ionization. Although 28 of the 59 VOCs were initially above detectable limits, none were found to be above detectable limits with air ionization. The TVOC reduction of 50% was encouraging given the very low total initial level of 112 µg/m^3 and the target performance level of 300

µg/m^3. The levels of 20 of the 59 specific VOCs were reduced and none were increased. No new VOCs were identified as products of incomplete ionization at the levels of detection.

Room air temperature ranged from 23.5 °C to 24.2 °C during the periods of test. The relative humidity ranged from 36.7% to 46.8%. The average concentration of carbon dioxide in an eight-hour period without ionization was 542 ppmv compared to a range of averages from 518 to 795 ppmv during three 8-h periods with ionization. This slight increase in carbon dioxide concentration was attributed to an increase in recirculated air and not to ionization products.

Indoor levels of ozone were measured continuously in this facility during operational periods with and without air ionization. The arithmetic average over a one-month operation without air ionization was 0.7 ppbv, with a maximum of 5.8 ppbv. This can be compared to a regulatory 8-h National Ambient Air Quality Standard (NAAQS) of 80 ppbv. The arithmetic average over a one-month operation with air ionization was 6.6 ppbv, with a maximum of 14.4 ppbv. Background levels in outside air were not measured directly, but were calculated to be in the range of 10–20 ppbv.

VIII. CONCLUSION

Air Ionization: Where We're Going To ...

"Chagrined a little that we have been hitherto able to produce nothing in this way of use to mankind; and the hot weather coming on, when electrical experiments are not so agreeable, it is proposed to put an end to them for this season."—Benj. Franklin, Esq., Letter IV, to Peter Collinson, F.R.S., "Farther Experiments and Observations in Electricity" (1751; reprinted in *Science*, vol. 123(3185), pp. 47–50, 13 Jan., 1956).

"No matter how sophisticated we believe we have become, there is much we do not know and considerably more we do not understand."—Dr. Stephen M. Kinne, "A Public Health Approach to Evaluating The Significance of Air Ions" (MS Thesis, University of Texas, Houston, [May 1997]).

Air ionization, although historically well documented and technologically well advanced, is just now entering the field of treatment of specific VOCs and PM$_x$ in indoor air environments. These applications are occurring in diverse areas, ranging from the removal of airborne contaminants in manufacturing operations involving sensitive materials, to the destruction of specific hazardous air contaminants in severely contaminated environments such as vehicular exhausts. Related technologies include oxidation in pulsed-corona reactors and other nonthermal plasma devices. The benefits of air cleaning by air ionization

are multiple: destruction, transformation, and removal of potentially hazardous VOCs and PM_x; elimination of odors; inactivation of microbials; extended and improved performance of conventional technologies (filtration and adsorption); low energy costs; minimal deposition of PM_x on surfaces; less hazardous reactants and byproducts; and the potential for possible associated health benefits.

Air Ionization: Recollections of the Past.

"We now know that every drop of rain falling on the ground or in the sea, and every drop of fresh water spray of a breaking wave, falling on a fresh water lake, sends negative electricity from the water surface to the air."—Lord Kelvin, "On the Electrification of Air" (*Science*, vol. 1(22), pp. 589–596, May 31, 1895).

"That slow chemical action accompanies various types of electrical discharge in many gases has been long known."—S.C. Lind, "The Theory of Chemical Action in Electrical Discharge" (*Science*, vol. 67(1745), pp. 565–569, June 8, 1928).

REFERENCES

[1] S. M. Kinne, "A public health approach to evaluating the significance of air ions," Health Science Center at Houston, School of Public Health, Univ. Texas,, Houston, TX, May 1997.

[2] M. N. Kondrashova, E. V. Grigigorreko, A. N. Tikhonov, T. V. Sirota, A. V. Temnov, I. G. Stavrovskaya, N. I. Kosyakova, N. V. Lange, and V. P. Tikonov, "The primary physico-chemical mechanism for the beneficial biological/medical effects of negative air ions," *IEEE Trans. Plasma Sci.*, vol. 28, pp. 230–237, Feb. 2000.

[3] A. P. Krueger and E. J. Reed, "Biological impact of small ions," *Science*, vol. 193, no. 4259, pp. 1209–1213, Sept. 24, 1976.

[4] F. Soyka and A. Edmonds, *The Ion Effect—How Air Electricity Rules Your Life and Health.* New York: E. P. Dutton, 1977, pp. 1–181.

[5] A. L. Tchijevsky, "Aeroionization: Its role in the national economy (Russia)," U.S. Office of Naval Intelligence, Washington, DC, 1960.

[6] A. Varga, "Fundamentals of electrobioclimatology, with special consideration of environmental health," in *Bioclimatic Significance of Air Ions.* Heidelburg, Germany: Springer–Verlag, 1981, ch. 5, pp. 307–398, 416.

[7] A. P. Wehner, "Air ions: Physical and biological aspects," in *History of Air Ion Research*, J. M. Charry and R. I. Kavet, Eds. Boca Raton, FL: CRC, 1987, ch. 9, pp. 1–538.

[8] J. R. Roth, "Industrial plasma engineering," in *Principles.* Philadelphia, PA: IOP, 1995, vol. 1, pp. 1–538.

[9] A. Schutze, J. Y. Jeong, S. E. Babayan, J. Park, G. S. Selwyn, and R. F. Hicks, "The atmospheric-pressure plasma jet: A review and comparison to other plasma sources," *IEEE Trans. Plasma Sci.*, vol. 26, pp. 1685–1694, Dec. 1998.

[10] H. Conrads and M. Schmidt, "Plasma generation and plasma sources," *Plasma Sources Sci. Technol.*, vol. 9, pp. 441–454, 2000.

[11] E. M. Van Veldhuizen, Ed., "Electrical discharges for environmental purposes: Fundamentals and applications," in *Nova Science* New York, 2000, pp. 1–432.

[12] A. Bogaerts, E. N. Neyts, R. Gijbels, and J. van der Mullen, "Gas discharge plasmas and their applications," *Spectrochim. Acta Part B*, vol. 57, no. 4, pp. 609–658, April.

[13] B. Eliasson and U. Kogelschatz, "Nonequilibrium volume plasma chemical processing," *IEEE Trans. Plasma Sci.*, vol. 19, pp. 1063–1077, Dec. 1991.

[14] U. Kogelschatz, B. Eliasson, and W. Egli, "From ozone generators to flat television screens: History and future potential of dielectric-barrier discharges," *Pure Appl. Chem.*, vol. 71, no. 10, pp. 1819–1828, 1999.

[15] B. M. Penetrante and S. E. Schulthesis, Eds., "Non-thermal plasma techniques for pollution control: Part A. Overview, fundamentals, and supporting technologies, part B," in *Electron Bean and Electrical Discharge Processing.* Berlin, Germany: Springer, 1993.

[16] L. A. Rosocha, "Processing of hazardous chemicals using silent-discharge plasmas," in *Plasma Science and the Environment*, W. Manheimer, Ed. Woodbury, NY: American Institute of Physics, 1997.

[17] E. H. W. M. Smulders, B. E. J. M. van Heesch, and S. S. V. B. van Paasen, "Pulsed power corona discharges for air pollution control," *IEEE Trans. Plasma Sci.*, vol. 26, pp. 1476–1484, Oct. 1998.

[18] K. Takaki, "Multipoint barrier discharge process for removal of NO_x from diesel engine exhaust," *IEEE Trans. Plasma Sci.*, vol. 29, pp. 518–523, June 2001.

[19] T. Yamamoto, "Optimization of nonthermal plasma for the treatment of gas streams," *J. Haz. Met. B*, vol. B67, pp. 165–181, 1999.

[20] M. Laroussi, "Biological decontamination by nonthermal plasmas," *IEEE Trans. Plasma Sci.*, vol. 28, pp. 184–188, Feb. 2000.

[21] M. Okubo, T. Kuroki, H. Kametaka, and T. Yamamoto, "Odor control using the AC barrier type plasma reactors," in *Proc. Industrial Applications Conf.*, vol. 2, 2000, pp. 868–875.

[22] K. H. Seo, B. W. Mitchell, P. S. Holt, and R. K. Gast, "Bactericidal effects of negative air ions on airborne and surface salmonella enteritidis from an artificially generated aerosol," *J. Food Protection*, vol. 64, no. 1, pp. 113–116, 2001, [Online] Available: http://www.seprl.ars.usda.gov/bmitchell/status.htm.

[23] R. Zhang, T. Yamamoto, and D. S. Bundy, "Control of ammonia and odors in animal houses by a ferroelectric plasma reactor," *IEEE Trans. Ind. Appl.*, vol. 32, pp. 113–117, Feb. 1996.

[24] H. W. Herrman, I. Henins, J. Park, and G. S. Selwyn, "Decontamination of chemical and biological warfare (CBW) agents using an atmospheric pressure plasma jet (APPJ)," *Phys. Plasmas*, vol. 6, pp. 2284–2289, May 1999.

[25] S. L. Daniels, "Engineered solutions for mitigation of IAQ problems," in *Proc. 2nd NSF Int. Conf. Indoor Air Health*, Miami Beach, FL, Jan. 29–31, 2001, pp. 243–249.

[26] ——, "Control of VOCs and PM_x in indoor environments by air ionization, poster presentation, electromed 2001," in *Proc. 2nd Int. Symp. Nonthermal Medical/Biological Treatments Using Electromagnetic Fields and Ionized Gases*, Portsmouth, VA, May 20–23, 2001.

[27] ——, "Applications of air ionization for control of VOCs and PM_x, paper #918," in *Proc. 94th Annu. Conf. Exhibition Air and Waste Management Assoc.*, Orlando, FL, June 24–28, 2001.

[28] S. L. Daniels and M. T. Fox, "Engineering design for indoor air environments: Perception vs. reality, Paper E-5," in *Proc. 1st NSF Int. Conf. Indoor Air Health: Impacts, Issues, and Solutions*, Denver, CO, May 3, 1999, pp. 65–74.

[29] S. L. Daniels and C. Frost, "Applications of negative air ionization for removal of volatile organic compounds (VOCs) and particulate matter (PM_x)," in *Proc. 2nd NSF Int. Conf. Indoor Air Health*, Miami Beach, FL, Jan. 29–31, 2001, pp. 346–52.

[30] A. M. Tyndall and G. C. Grindley, "The mobility of ions in air. Part I. Negative ions in moist air," *Proc. R. Soc. A*, vol. 110, no. 754, pp. 341–358, Feb. 1, 1926.

[31] J. A. Pollack, "The ions of the atmosphere," *Science*, vol. 29, no. 754, pp. 919–928, June 11, 1909.

[32] S. C. Lind, "The theory of chemical action in electrical discharge," *Science*, vol. 67, no. 1745, pp. 565–569, 1928.

[33] H. Tammet, *CRC Handbook of Chemistry and Physics.* Boca Raton, FL: CRC, 1997, pp. 14-30–14-32.

[34] P. B. Comita and J. I. Brauman, "Gas-phase ion chemistry," *Science*, vol. 227, pp. 863–869, Feb. 22, 1985.

[35] T. D. Bracken, "Small air ion properties," in *Air Ions: Physical and Biological Aspects*, J. M. Charry and R. I. Kavet, Eds. Boca Raton, FL: CRC, 1987, ch. 1, pp. 1–12, 205.

[36] I. Friedovich, "The biology of oxygen radicals," *Science*, vol. 201, pp. 875–880, 1978.

[37] F. Irwin, "Superoxide Anion Radical (O_2^-), Superoxide Dismutases, and Related Matters," *J. Biol. Chem.*, vol. 272(30), no. 18, pp. 515–518, 1997.

[38] M. N. Kondrashova, "Negative air ions and reactive oxygen species," *Biokhimiya*, vol. 64, pp. 361–363, 1999.

[39] I. Kruk, *The Handbook of Environmental Chemistry*, O. Hutzinger, Ed. New York: Springer, 1998, pt. I, vol. 2, pp. 1–261.

[40] K. U. Ingold *et al.*, "Oxidative Stress," Activities Rep., Steacie Inst. Molecular Sci., NRC-CNRC, Ottawa, Canada, 1999, [Online] Available: http://www.sims/nrc.ca/report99.pdf.

[41] V. P. Skulachev, "Biochemical Mechanisms of Evolution and the Role of Oxygen," [Online] Available: http://protein.bio.msu/su/biokhimiya/contents/v63/full/63 111 570.htm.

[42] N. I. Goldstein, R. N. Goldstein, and M. N. Merzlyak, "Negative air ions as a source of superoxide," *Int. J. Biometerol.*, vol. 36, pp. 118–122, 1992.

[43] O. Challenger, J. Braven, D. Harwood, K. Rosen, and G. Richardson, "Indoor air quality, part 1: Negative air ionization and the generation of hydrogen peroxide," *Sci. Total Environ.*, vol. 177, pp. 215–219, 1996.

[44] G. Richardson, D. J. Harwood, S. A. Eick, F. Dobbs, and K. G. Rosen, "Reduction of fine airborne particulates (PM3) in a small city centre office," *Sci. Total Environ.*, vol. 269, pp. 145–155, 2001.

[45] S. L. Daniels, "Products of incomplete combustion, (O_x, CO_x, HO_x, NO_x, RO_x, MO_x, and PO_x)," *J. Hazardous Mater.*, vol. 22, pp. 161–173, 1989.

[46] ——, "Interactions of volatile organic compounds and particulates—Speciation of copollutants in indoor and outdoor air environments for risk assessment," in *Proc. Odors and VOC Emissions Conf.*, Cincinnati, OH, Apr. 16–19, 2000.

[47] G. R. Peyton, M. A. Smith, and B. M. Payton, "Photolytic ozonation for protection and rehabilitation of groundwater resource: A mechanistic study," Illinois State Water Survey, Univ. Illinois, Champaign, IL, Water Resources Center Res. Rep. 206, Jan. 1987.

[48] W. A. Jacoby, D. M. Blake, J. A. Fennell, J. E. Boulter, L. M. Vargo, M. C. George, and S. K. Dolberg, "Heterogeneous photocatalysis for control of volatile organic compounds in indoor air," *J. AWMA*, vol. 46, pp. 891–898, 1996.

[49] G. C. Morrison and C. J. Howard, "Examination of indoor chemistry using chemical ionization mass spectroscopy," in *Proc. 94th Annu. Conf. Exhibition, Air and Waste Management Assoc.*, Orlando, FL, June 25, 2001.

[50] A. S. Yen, S. S. Kim, M. H. Hecht, M. S. Frant, and B. Murray, "Evidence that the reactivity of the martian soil is due to superoxide ions," *Science*, vol. 289, no. 5486, pp. 1909–1912, Sept. 15, 2000.

[51] E. Stoffels, W. W. Stoffels, D. Vender, M. Kando, G. M. W. Kroesen, and F. J. de Hoo, "Negative ions in a radio-frequency oxygen plasma," *Phys. Rev. E*, vol. 51, no. 3, pp. 2425–2435, 1995.

[52] E. Stoffels, W. W. Stoffels, and G. M. W. Kroesen, "Plasma chemistry and surface processes of negative ions," *Plasma Sources Sci. Technol.*, vol. 10, pp. 311–317, 2001.

[53] J. M. Weber, J. A. Kelly, S. B. Nielsen, P. Ayotte, and M. A. Johnson, "Isolating the spectroscopic signature of a hydration shell with the use of clusters: Superoxide tetrahydrate," *Science*, vol. 287, no. 5462, pp. 2461–2463, Mar. 31, 2000.

[54] C. J. Weschler and H. C. Shields, "Potential reactions among indoor pollutants," *Atmos. Environ.*, vol. 31, no. 21, pp. 3487–3495, 1997.

[55] L. N. Krasnopernov and L. G. Krishtopa, "Kinetic and mechanism of hydrocarbons transformation in dielectric barrier corona discharge," in *Proc. 5th Int. Conf. Chemical Kinetics*, vol. 20. Gaithersburg, MD, July 2001, [Online] Available: http://www.cstl.nist.gov/div838/kinetics2001/agenda/j_session/j7/j7.htm, pp. 16–20.

[56] M. A. Malik, A. Ghaffar, and S. A. Malik, "Water purification by electrical discharges," *Plasma Source Sci. Technol.*, vol. 10, pp. 82–91, 2001.

[57] S. Futamura, A. H. Zhang, and T. Yamamoto, "The dependence of nonthermal plasma behavior of VOCs on their chemical structures," *J. Electrostat.*, vol. 42, pp. 51–62, 1997.

[58] B. M. Penetrante, M. C. Hsiao, J. N. Bardsley, B. T. Merritt, G. E. Vogtlin, A. Kuthi, C. P. Burkhart, and J. R. Bayless, "Identification of mechanisms for decomposition of air pollutants by nonthermal plasma processing," *Plasma Sources Sci. Tech.*, vol. 6, no. 3, pp. 251–259, 1997.

[59] F. Pontiga, C. Soria, and A. Castellaanos, "Electrical and chemical model of negative corona in oxygen at atmospheric pressure," *J. Electrostat.*, vol. 40 and 41, pp. 115–120, 1997.

[60] T. Yamamoto, "VOC decomposition by nonthermal plasma processing—A new approach," *J. Electrostat.*, vol. 42, pp. 227–238, 1997.

[61] "Fundamental Challenges in Electron-Driven Chemistry," National Energy Res. Sci. Comput. Center, Lawrence Berkeley National Laboratory,, Oct. 9–10, 1998, [Online] Available: http://www.lbl.gov/ICSD/mccurdy/workshop_final_1.html.

[62] C. Nunez, G. H. Ramsey, W. H. Ponder, J. H. Abbott, L. E. Hamel, and P. H. Kariher, "Corona destruction: An innovative control technology for VOCs and air toxics," *Air Waste*, vol. 43, pp. 242–247, 1993.

[63] S. G. Lias and E. J. Bartmess, "Gas-phase ion thermochemistry," in *NIST Chemistry WebBook*. Gaithersburg, MD: Nat. Inst. Standards Technol., [Online] Available: http://webbook.nist.gov/chemistry/.

[64] R. McAdams, "Prospects for nonthermal atmospheric plasmas for pollution abatement," *J. Phys. D, Appl. Phys.*, vol. 34, pp. 2810–2821, 2001.

[65] "Residential Air Cleaning Devices: Types, Effectiveness and Health Impact," American Lung Association, New York, Jan. 1997, [Online] Available: http://www.lungusa.org/air/air00_aircleaners.html.

[66] "Residential Air Cleaning Devices: A Summary of Available Information," Tech. Rep. EPA 400/1-90-002, U.S. EPA, Office of Air and Radiation (OAR), Washington, DC, Feb. 1990, [Online] Available: http://www.epa.gov/iaq/pubs/ozonegen.html.

[67] J. Priest, J. McLaughlin, L. Christianson, A. Zhivov, M. McCulley, G. Chamberlin, M. Tumbleson, R. Maghirang, B. Shaw, Z. Li, J. Arogo, and R. Zhang, "Ventilation technology systems analysis," Tech. Rep. EPA-600/R-95-065, U.S. EPA, Washington, DC, May 1995.

[68] J.-S. Chang, P. A. Lawless, and T. Yamamoto, "Corona discharge processes," *IEEE Trans. Plasma Sci.*, vol. 19, pp. 1152–1166, Dec. 1991.

[69] K. Urashima and J.-S. Chang, "Removal of volatile organic compounds from air streams and industrial flue gases by nonthermal plasma technology," *IEEE Trans. Dielect. Elect. Insulation*, vol. 7, pp. 602–614, May 2000.

[70] P. A. Lawless, A. S. Viver, D. S. Ensor, and L. E. Sparks, "Computations on the performance of particle filters and electronic air cleaners," in *Proc. Indoor Air '90*, vol. 3, Toronto, Canada, 1990, pp. 187–192.

[71] M. Lippman, "Health effects of ozone: A critical review," *J. APCA*, vol. 39, pp. 672–695, 1989.

[72] R. J. Shaughnessy and L. Oatman, "The use of ozone generators for the control of indoor air contaminants in an occupied environment," in *Proc. Indoor Air '91*, Atlanta, GA, 1992, pp. 318–324.

[73] M. F. Boeniger, "Use of ozone generating devices to improve indoor air quality," *Amer. Indust. Hyg. Assoc. J.*, vol. 56, no. 6, pp. 590–598, 1995.

[74] W. Daniell, J. Camp, and S. Horstman, "Trial of a negative ion generator device in remediating problems related to indoor air quality," *J. Occup. Med.*, vol. 33, no. 6, pp. 681–687, 1991.

[75] R. J. Shaughnessy, E. Levetin, J. Blocker, and K. L. Sublette, "Effectiveness of portable indoor air cleaners: Sensory testing results, indoor air," *J. Int. Soc. Indoor Air Quality Clim.*, vol. 4, pp. 179–188, 1994.

[76] E. Esswein and M. F. Boeniger, "Effect of an ozone-generating air-purifying device on reducing concentrations of formaldehyde in air," *Appl. Occup. Hyg.*, vol. 9, no. 2, pp. 139–146, 1994.

[77] W. W. Nazaroff and G. R. Cass, "Mathematical modeling of chemically reactive pollutants in indoor air," *Environ. Sci. Tech.*, vol. 20, pp. 924–934, 1986.

[78] T. Salthammer and S. Kephalopoulos, "Assessment of material emissions on IAQ, state-of-the-art review," in *Proc. Healthy Buildings Conf.*, Espoo, Finland, Aug. 6–10, 2000, [Online] Available: http://www.hb2000.org/workshop29.html.

[79] R. J. Shaughnessy, T. J. McDaniels, and C. J. Weschler, "Indoor chemistry: Ozone and volatile organic compounds found in tobacco smoke," *Environ. Sci. Tech.*, vol. 35, pp. 2758–2754, 2001.

[80] J. J. Coogan and A. D. Sappey, "Distribution of OH within silent discharge plasma reactors," *IEEE Trans. Plasma Sci.*, vol. 24, pp. 91–92, Feb. 1996.

[81] Z. Falkenstein and J. J. Coogan, "Microdischarge behavior in the silent discharge of nitrogen-oxygen and water-air mixtures," *J. Phys. D, Appl. Phys.*, vol. 30, pp. 817–825, 1997.

[82] B. Eliasson, M. Hirth, and U. Kogelschatz, "Ozone synthesis from oxygen in dielectric barrier discharges," *J. Phys. D, Appl. Phys.*, vol. 20, no. 11, pp. 1421–1437, Nov. 14, 1987.

[83] K. Yan, H. Hui, M. Cui, J. Miao, X. Wu, C. Bao, and R. Li, "Corona induced nonthermal plasmas: Fundamental study and industrial applications," *J. Electrostat.*, vol. 44, pp. 17–39, 1998.

[84] K. Yan, E. J. M. van Heesch, A. J. M. Pemen, and P. A. H. J. Huijbrechts, "From chemical kinetics to streamer corona reactor and voltage pulse generator," *Plasma Chem. Plasma Process*, vol. 21, no. 1, pp. 107–127, 2001.

[85] R. J. Van Brunt, "Stochastic properties of partial-discharge phenomena, review," *IEEE Trans. Elect. Insulation*, vol. 26, pp. 902–948, Oct. 1991.

[86] ——, "Physics and chemistry of partial discharge and corona, 1994 whitehead memorial lecture," *IEEE Trans. Dielect. Elect. Insulation*, vol. 1, pp. 761–784, May 1994.

[87] B. Eliasson and U. Kogelschatz, "Modeling and applications of silent discharge plasma," *IEEE Trans. Plasma Sci.*, vol. 19, pp. 309–323, Apr. 1991.

[88] U. Kogelschatz, "Diagnostics of nonequilibrium high pressure plasmas," in *Proc. APP Spring Meeting*, Bad Honnef, Germany, Feb. 18–21, 2001.

[89] N. Gherardi and F. Massines, "Mechanisms controlling the transition from glow silent discharge to streamer discharge in nitrogen," *IEEE Trans. Plasma Sci.*, vol. 29, pp. 536–544, June 2001.

[90] J. Guikema, N. Miller, J. Niehof, M. Klein, and M. Walhout, "Spontaneous pattern formation in an effectively one-dimensional dielectric-barrier discharge system," *Phys. Rev. Lett.*, vol. 85, no. 18, pp. 3817–3820, Oct. 30, 2000.

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