SOME ASPECTS OF METALLIC ION CHEMISTRY AND DYNAMICS
IN THE MESOPHERE AND THERMOSPHERE

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The relationship between the formation of "sporadic" layers of metallic ions and the "dumping" of these ions into the upper mesosphere is discussed in terms of the tidal winds, "classical" (i.e., windshear) and other more complex, perhaps highly non-linear layer formation mechanisms, and a possible circulation mechanism for these ions. Optical, incoherent scatter radar, rocket, and satellite derived evidence for various layer formation mechanisms and for the metallic ion circulation system is reviewed. The results of simple one-dimensional numerical model calculations of sporadic E and intermediate layer formation are presented along with suggestions for more advanced models of intense or blanketing sporadic E. The flux of metallic ions "dumped" by the tidal wind system into the mesosphere is estimated and compared with estimates of total particle flux of meteoric origin. Possible effects of the metallic ion flux and of meteoric "dust" on D region ion chemistry are discussed.

I. Introduction

That meteors "burn-up" in the 80-110 km region of the atmosphere is unquestioned. However, the effect of this mass flux on the upper atmosphere and how the meteoric debris eventually settles to the ground is very much in question. The mass flux is estimated to be $10^{-10}$ gm-cm$^{-2}$-s$^{-1}$ or 44 metric tons per day over the earth (HUGHES, 1978; HUNTEN et al., 1980) and, after meteor burn-up, is observable only in atomic neutral and ionized forms or as dust or "smoke" (HUNTEN et al., 1980) particles. The "budgets" or aeronomy of these two forms is unknown. It is the purpose of this paper to explore the budget issue for the atomic metal ions which form into narrow (in height) layers known as sporadic E and to introduce some possible new "clues" concerning dust in the meteor zone.

Numerous rocket borne mass spectrometer measurements (eg. AIKIN and GOLDBERG, 1973; Zbinden et al., 1975) have demonstrated the presence of atomic metal ions in sporadic E layers. These results have been confirmed by incoherent scatter radar measurements (eg. BEHNKE and VICKERY, 1975; TEPLY and MATHEWS, 1985), by passive optical measurements (eg. TEPLY et al., 1981) and by Lidar measurements (eg. GRANIER et al., 1984). Also Mg$^+$ and Fe$^+$ have been observed at F region altitudes (eg. GREBOWSKY et al., 1978; MENDE et al., 1985) leading to much speculation regarding the transport of these ions from the deposition region to these heights. MATHEWS and BEKENY (1979) have proposed an E/F region circulation mechanism involving tides, the equatorial fountain effect (HANSON et al., 1972), and "sporadic" layers which may explain some observations.
Sporadic E layers are transported to the lower thermosphere where chemistry (eg. 3 body recombination of the ions; SWINDER, 1984; BROWN, 1973) becomes dominant over transport (MATHews and BEKEnY, 1979). Simple chemistry, such as the ion/neutral concentration ratio of a species, can be investigated experimentally. For example, neutral iron and calcium have been observed below 100 km altitude by passive optical means (TEPLEY et al., 1981 a,b) and LIDAR (GRANIER et al., 1984) respectively. However, the formation and growth mechanisms of dust or smoke particles which ultimately settle out of the atmosphere have proved much more difficult to investigate and evaluate in terms of overall effect on the mesosphere and D region. Dust quite probably plays a major role in noctilucent cloud formation (TURCO et al., 1982) and possibly modifies D region ion chemistry (eg. PARTHASARATHY, 1976).

In section 2 we explore some aspects of metallic ion transport at mid and low latitudes while section 3 emphasizes some aspects of metallic ion and dust chemistry. Section 4 forms a summary and discussion of the above topics from which we conclude that metals and dust should be studied via combined lidar and incoherent scatter radar instrumentation.

The basic veracity of the "wind shear" theory of layer formation (CHIMONAS and Axford, 1968; WHITEsteAD, 1971) is unquestioned (MATHews and BEKEnY, 1979) as is the fact of metal ions (Fe⁺, Mg⁺, Ca⁺, Si⁺, etc.) within at least the 90-120 km layers.

II. Sporadic Layers and Metal Ion Transport

Figure 1 shows a typical time series of electron concentration profiles obtained with the Arecibo 430 MHz Incoherent Scatter Radar (ISR). All the major features of midlatitude "sporadic" layers appear in this sequence of profiles. In particular three layers (A,B,C) display the highly time coherent behavior that has been linked to the diurnal and semidiurnal tides (MATHews and BEKEnY, 1979). More important to this paper is that layers B and C are the so-called intermediate layers (FUJITAKA and TOHMATSU, 1973) which descend from the F region into the E region where these layers join the sporadic E system.

Another idea of layer behavior observed at Arecibo is given in Fig. 2 where layer height is plotted versus time without regard to layer "strength" for three full days. The major features seen in Fig. 2 confirm those of Fig. 1. That is, intermediate layers descend from the F region, join the sporadic E layer system and finally descend to the "dumping" zone at 90 km altitude. This behavior is typical for Arecibo and two major points emerge. These are that ion layers are not sporadic but are almost always present and that the net vertical ion motion in the tidal wind is downward. That is, ions can move upward but only to the next descending convergent node (MATHews and BEKEnY, 1979).

Figures 1 and 2 deal, by nature of the observing technique, only with vertical layer motion. We see that minimum layer "travel time" from 150 km to 90 km is about 18 hours where rates of 4-8 km/hr above 110 km and of 0.5 - 1 km/hr below 100 km correspond to semidiurnal and diurnal tidal phase speeds respectively.
Electron concentration is plotted on a logarithmic scale (ordinate) versus altitude (abscissa) and time (separate profiles arrayed along the ordinate with times ranging from 1415 through 2320 hours). These data were obtained with the Arecibo 4430 MHz incoherent scatter radar and the arrows indicate the $10^4$ el/cc level on each profile. Note the three separate long-lived layers (A, B, C) and the various descent rates. The early portion of layer B and layer C are known as intermediate layers. (Figures from MATHEWS and BEKENY, 1979).
The altitude of peak concentration of ion layers is plotted (for all layers) versus time for three days of Arecibo observations. The formation of layers and the rate of descent is controlled by the diurnal and semidiurnal tides. That several intermediate layers per day are observed indicates the presence of multiple semidiurnal modes.
Figure 3 summarizes the basis for layer formation via the $V \times B$ mechanism. That is, below about 130 km altitude ions are sufficiently coupled, via collisions, to the neutral atmosphere that a node in the zonal tidal wind system accumulates long-lived ions if the westward wind is above and eastward wind below. This "convergent" node in the zonal system also corresponds to maximum southward wind (northern hemisphere). Thus, the layers depicted in Figures 1 and 2 are being transported toward the equator at speeds of the order of 100 m/sec (MATHEWS, 1976; HARPER, 1977) or 360 km/hr. It is thus possible that these metallic ions are, at least at some longitudes, (the earth's spin and magnetic axes are not aligned) brought close enough to the magnetic equator to come under the influence of the combined polarization electric fields and $E \times B$ drifts which can lift them to the F region. This vertical transport effect is known as the equatorial fountain effect (HANSON et al., 1972) and is invoked in order to explain the metal ions observed in the F region at magnetic dip latitudes between $\pm 30^\circ$ (MENDE et al., 1985; FENSEN and HAYS, 1982).

The "fountain effect" is a two part process. The first part of the process is the lifting by the vertical polarization electric field of the minor constituent metal ions from the 90-110 km region to the lower F region. The second part of the process is the further lifting of these ions via $E \times B$ drift into the mid- and upper F region. The ions are then free to diffuse and fall along the B field lines to higher latitudes. This process is depicted in Fig. 4 (HANSON and MOFFETT, 1966).

The equatorial E region vertical polarization electric field arises from the fact that the vertical electron mobility is much larger than the corresponding ion mobility. Thus the primary zonal ("Pedersen") electric field gives rise to the "Hall" or vertical polarization E field. The Hall field produces a zonal current which combines with the original Pedersen current producing the eastward equatorial electrojet (Cowling) current (WOODMAN et al., 1977; VOLLAND, 1984; section 9.6). Note that this lifting mechanism only operates during the daylight hours. The reverse electrojet, which occurs from late afternoon through to sunrise, is characterized by a downward rather than upward polarization electric field.

The $E \times B$ lifting mechanism becomes dominant at about 160 km altitude where electron and ion collision frequencies become small relative to respective cyclotron frequencies and the vertical polarization field tapers off. The electric field is the "normal" daytime eastward E region field which is mapped along B field lines to the F region. (MARTYN, 1955; VOLLAND, 1984; Section 9.7).

The total time for transport of metal ions from the equatorial E region to the higher latitudes (within $\pm 30^\circ$ magnetic latitude) of the F region must not exceed about 12 hours if the entire "circulation" process is to occur during the time the fountain effect is operative. This requirement seems unnecessary in that the "reverse fountain effect" which occurs when the daytime eastward E field reverses to the west is weaker than the daytime fountain (WOODMAN et al., 1977) thus leading to an apparent daily net positive flux of metal ions into the equatorial F region from the equatorial E region. Some evidence for this "pulsed" source of metal ions is found in the observed "clouds" of Mg reported by MENDE et al., (1985) and possibly by KUMAR and HANSON (1980).
Fig. 3 A schematic representation of the "windshear" or $V \times B$ mechanism for layer formation. The earth's magnetic field $B$ is directed from south to north. Note that in the northern hemisphere the "convergent" node in the zonal tidal wind system corresponds to a maximum southward wind.
Fig. 4  The meridional plasma drift due to electric and gravitational fields. This drift pattern would carry metal ions from the equatorial F region to magnetic latitudes as high as Arecibo. The metal ions are transported to the equatorial F region via the "fountain effect".  [after HANSON and CARLSON, 1977 and HANSON and MOFFETT, 1966].
Finally, we investigate some of the properties of the intermediate layer system shown in Figure 2. This system originates with the F region meridional winds (because the plasma is constrained to move parallel to the B field) where a northward wind above and southward wind below yields a "convergent node". At Arecibo, the F region winds are semidiurnal in character (HARPER, 1977). HARPER notes the twice-per-day formation of the intermediate layer at the "base" of the F region. (Note that Figure 2 shows a more complicated situation due apparently to multiple semidiurnal tidal modes.) He further notes that any metallic ions in the 120-250 km region will be swept into the nearest descending convergent node of the tidal wind system. The formation of intermediate layers in the F region is seen in Figure 8 of HARPER (1977) which is reproduced here as Figure 5.

In Figure 5, we see the basic features of the intermediate layer behavior. That is, winds are moving the F region up and down throughout the night with strong convergent nodes characterizing the actual intermediate layer. The "morning" intermediate layer is actually associated with the descent of the F layer which begins at about 0100 hrs. Also note that here again the 100 km sporadic layer descends and decays away through the night.

We conclude this section by asserting that any metal ions present at Arecibo latitudes in the F region will be swept into the E region by the wind system which forms the intermediate layer. This F to E region transport process then completes the hypothesized metal ion circulation system (MATHEWS and BEKENY, 1979).

III. Aspects of Layer Chemistry

SHEN et al., (1976) consider both photionization and transport in the formation of the intermediate layers observed in Arecibo. They conclude that these layers are not supportable in the 130-160 km E region without a production rate of 1-5 cm$^{-3}$s$^{-1}$ and/or metallic ions. The suggested production rate is significantly higher than expected for scattered EUV (FUJITAKA et al., 1971) and, as noted in the last section, at least the continual presence of metal ions remains conjectural.

Thus, while the MENDE et al., (1985) results seem to indicate "clouds" of Mg$^{+}$ which extend from the E to F region and TEPLEY et al., (1981a) reports Ca$^{+}$ in an intermediate layer it is appropriate to further investigate standard (non-metallic) chemistry in the intermediate layer. WEBSTER (1981) has done this via a 2 ion, 1 dimensional chemical-dynamical numerical model of the 110-510 km ionosphere. This model, while simple, contains all the features necessary to investigate the formation, maintenance, and transport of the intermediate layer. The molecular ions NO$^{-}$ and O$^{-}$ are combined into a single effective molecular ion. The nighttime scattered EUV photoionization production sources for NO$^{-}$/O$_2$$^+$ and O$^{-}$ are based on the model of FUJITAKA et al., (1971) and all sources of either NO$^{-}$, O$_2$$^+$, or O$^{-}$ (eg N$_2$$^+$) are included. A proton-oxygen charge exchange source of O$^+$ based on the Young et al., (1979) results is also included as is a model of the Arecibo semidiurnal tide.

Results from this numerical model are given in Figure 6 which for display purposes is similar in format to Figure 5. In Figure 6 the
Fig. 5 A three-dimensional presentation of electron concentration plotted on a logarithmic scale versus height and time. Evening and morning intermediate layers are seen to form at the base of the F layer. Note the wavelike motions of the F layer. [From Figure 8; HARPER, 1977 and Figure 5; SHEN et al., 1976].
Fig. 6 Model calculations of the formation of an intermediate layer using the nighttime EUV production model of FUJITAKA et al., (1971) and an Arecibo-like semidiurnal wind. This model layer contains only NO²⁻/O²⁺ and O⁺ ions as discussed in the text.
intermediate layer, which is composed of both \( \text{NO}^+ / \text{O}_2^+ \) and \( \text{O}^+ \), "detaches" from the base of the F layer (note the height scale change at 180 km) and descends to the nighttime E layer. This model intermediate layer has a peak electron concentration of 1000-2000 el/cc and a full width of about 10 km in altitude.

The basis for formation of this layer is that \( \text{NO}^+ / \text{O}_2^+ \) ions have 1-2 hour lifetimes away from the layer. Thus convergent vertical ion "winds" of even 5m/sec can sweep ions into the layer form 25 km above or below the layer. Ion lifetime in the layer is less than 10 minutes at the layer peak.

The ion-electron production rate in this model calculation is essentially that shown in Figure 2 of FUJITAKA et al., (1971). That is a local maximum total production rate of 0.5 cm\(^{-3}\) s\(^{-1}\) at 180 km altitude, a local minimum rate of 0.2 cm\(^{-3}\) s\(^{-1}\) at 105 km altitude, and a peak rate of 2 cm\(^{-3}\) s\(^{-1}\) at 105 km altitude. Thus these rates are sufficient to cause the formation of an intermediate layer which would be observable by the Arecibo radar. However, the more intense intermediate layers studied by SHEN et al., (1976) apparently require much larger production rates of metal ions. No sustained source for the high production rate is known, thus the Figure 6 model calculations suggest that indeed metal ions were present in the layers studied by SHEN et al., (1976).

Clearly metal ions could have been added to the model calculations just described resulting in even more intense intermediate layers. Then, however, the question of altitude distribution of metallic versus molecular ions within an intermediate or sporadic E layer arises. Specifically the long-lived metallic ions are swept to the center of the layer where the resultant increase in electron concentration would decrease molecular ion lifetime against recombination. Thus we expect the presence of metallic ions within layers to "sharpen" the layer peak and perhaps lead to more intense sporadic E.

The combined effect of metallic and molecular ions on layer formation in the 90-130 km altitude region has been investigated by TUCKER (1983) using a numerical model similar to that of WEBSTER (1981). This model also employed the EUV production model of FUJITAKA et al., (1971) while the wind system used was that of MATHEWS and BEKENY (1979). Figure 7 is a three dimension view (electron concentration versus height and time) of a two layer system superimposed on the "background" nighttime E layer. This results is "typical" for Arecibo in that the sporadic E layer appears at the lower heights while two intermediate layers form at the upper boundary, descend, and join. The broad distribution of ionization in Figure 7 is the normal nighttime E layer.

Chemical and dynamical effects in this model are better seen by plotting molecular and metallic ion concentration separately. This is done in Figures 8 and 9 which display the molecular and metallic ion profiles respectively, corresponding to Figure 7. From Figure 8 we see that at higher heights the intermediate layers are composed of molecular ions while at lower heights a "trench" in molecular ion concentration occurs at the layer peak. This "trench" corresponds to a maximum in metallic ion concentration as seen in Figure 9. This model was "started" with an even
Fig. 7 Model electron concentration is plotted versus height and time. The FIJITAKA et al. (1971) nighttime production source and the MATHEWS and BEKENY (1979) diurnal and semidiurnal tidal wind system were used in these calculations which cover 26 hours with each contour separated by 4000 sec. The nighttime production source was used for the whole calculation so as to not mask layer dynamics for this presentation. Note the sporadic E layer at 105 km and below and the two intermediate layers which join at 110 km and at middle times.
Fig. 8 The molecular ion concentration corresponding to the model results shown in Figure 7. Note that molecular ion concentration is depressed at the center of the large layers shown in Figure 7. This is due to the enhanced electron-molecular ion recombination rate in the layer.
Fig. 9 The metallic ion concentration corresponding to the model results shown in Figure 7. The initial 100 metal ions per cc are seen to form into highly peaked "sporadic" layers.
distribution of metal ions \((10^2 \text{cm}^{-3})\) so that once these ions accumulated in layers no additional metallic ions were available to, for example, enhance the peak concentration of the second intermediate layer.

An important result of these calculations is seen in Figure 10 which is a "cross-section" of Figure 7. From Figure 10 it is clear that the metal ion layers substantially depress molecular ion concentrations at the center of the layer. Also, the molecular ions at layer edges help support the layer against diffusion resulting in somewhat narrower and more intense layers when compared with the metal ion only case. However, this molecular ion enhancement of sporadic layers, in which metal ion diffusion is slowed by the molecular ion layer edges, in no way explains the very intense sporadic E events which are often observed at Arecibo and elsewhere. These events are apparently due to some other physical process (eg. local horizontal currents) which sufficiently counteract diffusive forces.

We have discussed the roles of chemistry and dynamics in the formation and maintenance of intermediate and sporadic E layers. These layers are a manifestation of the mechanism by which metallic ions maybe transported to, from, and across the meteor source region. We turn next to mechanisms by which metallic ions are finally lost from the 90 km and above region. An example of this loss process is seen in Figures 1, 2, and 5 where the very low lying sporadic layers are "dumped" at about 90 km altitude. This process is particularly evident in Figure 2 at 90 km and zero hours where on each day the diurnal tide dumps the layer.

The "dumping" of metallic ions into the 90 km altitude region is discussed by MATHEWS and BEKENY (1979) and occurs when the vertical ion velocity becomes less than the tidal phase velocity resulting in the layer being left behind as the tidal mode descends. The "dumped" layer then dissipates because of diffusion, electron-ion recombination, or possibly because of attachment of electrons to dust forming negative ions. Formation of stable molecular negative ions by the "usual" chemical paths is not thought to be effective above 85 km altitude even at night (eg. GANGULY, et al., 1979).

Recombination becomes an efficient loss mechanism when atmospheric pressure is high enough for three body (neutral reactant (eg. 0), atomic ion, third particle) reactions (BROWN, 1973; BANKS and KOCKARTS, 1973; Section 9.2) to occur. Three body reactions lead to the formation of metal based molecular ions (eg. BROWN, 1973; Table 10) and are efficient below 100 km altitude. These ions can then recombine with electrons or participate in other chemistry.

Model calculations (MURAD, 1978; TEPLEY, 1981) indicate that concentration ratio of molecular metal ions (eg MO+, MN2+ etc.) to parent ion are small at all heights above 80 km altitude. That is while these ions form they are rapidly converted to neutral species via electron recombination (eg. MO2+ + e \rightarrow M + O2) or to other ion forms. MURAD (1978) argues that detection of metal oxide ions by rocket mass spectrometric measurements (see MURAD for references) is probably invalid due to hydrocarbon contamination of the instruments. A further possibility that atomic or molecular metal ions attach directly to dust or meteoric smoke particles will be discussed shortly.
Fig. 10 Concentration cross-section of Figures 7, 8, and 9 at $t = 14.5$ hours. The short dashed line is the metal ion concentration etc. The presence of the molecular ions supports a somewhat narrower more intense (10-20%) metal ion layer that could exist otherwise.
Combined three body and two body reactions leading to neutral atomic metal and metal compounds then appear to be the major sink for atomic metal ions with the possible exception of direct attachment to dust. Fortunately ground based remote sensing of the metal ion-to-neutral ratio is possible. TEPLEY, et al. (1981 a,b) reports on separate Ca" and Fe concentration determinations via twilight resonant scattering of sunlight while GRANIER, et al., (1984) report almost simultaneous common value lidar measurements of Ca and Ca" concentration profiles. The GRANIER, et al. results are given in Figure 11.

All available evidence indicates that the atomic metal ion-to-neutral concentration ratio reaches one between 90 km and 100 km altitude and increases rapidly with increasing altitude. Also a modest "reservoir" of neutral atomic metals appears to be centered at 85-90 km altitude. Two important results seen in Figure 11 are the similar but displaced Ca and Ca" profiles and that the Ca concentration profile decreases sharply on the layer bottomside. The Figure 11 Ca" results are similar to those expected based on incoherent scatter radar total layer metal ion (i.e., electron) concentration measurements and the distribution of the elements in the average meteor. Lidar and combined lidar/incoherent scatter radar measurements will in the future add considerably to our knowledge of metal ion chemistry in the "dumping" region.

While the chemical mechanisms are probably many and uncertain it does seem clear that the neutral atomic metals become involved in reactions leading ultimately to the formation or growth of the meteoric "smoke" particles of HUNTEST, et al., (1980). HUNTEST estimates the concentration of the smoke particles to be ~ 1000 cm"3 and that this concentration falls off rapidly above 90 km altitude. As an estimate of the importance of meteoric mass appearing directly as smoke relative to ionized forms transported in layers we note that estimated meteoric mass influx of 44 metric tons per day corresponds to a particle flux of ~ 10^6 cm^-2s^-1 mass 57 amu atoms^-3 and a vertical speed of 10^-cm/sec or a particle flux of ~ 10^6 cm^-2s^-1 also. The sporadic E layer arrives at 90 km altitude over only one or two hours per day. However, the point remains that at least sometimes meteoric ion flux in sporadic layers probably equals total meteor mass flux at 90 km altitude. The ion flux from sporadic layers may then influence the growth or even formation of the smoke particles while the dust or smoke particles possibly effect the ion chemistry.

HUNTEST takes the minimum size of the smoke particles to be a radius of 2A with a maximum density of 4 gm cm^-3 corresponding to a particle mass of 80 amu. As the smoke particle grows it falls through the atmosphere until for a variety of reasons it is brought to the surface.

We are concerned with the role of meteoric smoke not only as a "sink" for atomic metals but also as an influence on the aeronomy of the meteor zone. Dust has long been considered important to the formation of noctilucent clouds at high latitudes. TURCO et al., (1982) extensively treats the problem of noctilucent cloud formation including effects of ion attachment to dust or ice particles. PARTHASARATHY (1976) has considered dust a direct "sink" for D region ionization. We will dwell on the latter
Fig. 11 Profiles of Ca and Ca$^+$ concentration obtained by LEDAR at the Observatoire de Haute Provence and reported by GRANIER et al., (1984).
as noctilucent clouds are not an aspect of low and mid-latitude D region aeronomy.

The role of dust in ion chemistry is of interest not only as a possible mechanism for growth of dust by accumulation of metals in both ion and neutral form but also because of associated possible effects on the "normal" molecular (NO, O₂) and atomic metal ion chemistry near 90 km altitude. Dust particles presumably effect ion chemistry simply by successive capture of ions and electrons and possibly by photoelectric emission of electrons from the dust particles. Parthasarathy finds dust effects significant only if dust concentrations are large (> 1 cm⁻³); however, he considers only very massive dust particles (~ 10⁴ amu).

HUNTEN et al., (1980; Figures 4 and 5) treat a spectrum of particle sizes. For initial smoke particles of radius 2A (~ 80 amu) peak dust concentrations of 5 × 10⁴ cm⁻³ are predicted for 85 km altitude while for 10A radius (~ 10⁴ amu) a peak concentration of 3 × 10⁴ cm⁻³ is predicted for 80 km altitude. The corresponding surface areas per unit volume (A) of the dust are 10⁻² cm²/cm³ and 7 × 10⁻² cm²/cm³ respectively. The mean time between collisions (Maxwellian velocity distribution) assuming uncharged dust and neutral atoms or molecules is \( t = \frac{4}{9} \sqrt{2} \frac{v}{kT/m} \), where \( v \) is the thermal velocity, \( k \) is Boltzmann's constant, \( T \) is absolute temperature, and \( m \) is the mass of colliding atom or molecule) or about two days at 90 km altitude. The mean time between attachment events for a single electron with dust would clearly be much faster (~ 15 minutes) using the above formula. However, the induced dipole moment would significantly increase the collision rate of electron and ions with uncharged dust.

We thus expect the dust or smoke particles to effect neutral atomic metals or metal compounds on the time scale of a day or two. For example at the peak Ca concentration of 10⁵ cm⁻³ in Figure 11 the collision rate is 5 × 10⁻⁴ cm⁻³ s⁻¹. However, in a 90 km sporadic layer of peak electron concentration 10⁴ cm⁻³ the ion collision rate with would be 5 × 10⁻⁴ cm⁻³ s⁻¹ and the electron collision rate would be 10⁻⁸ cm⁻¹ s⁻¹. The three body reaction producing metal dioxides (rate 2.5 × 10⁻⁸ cm⁻³ s⁻¹ for iron; BROWN, 1973) would have a reaction rate of 25 cm⁻³ s⁻¹ at 90 km assuming 10⁴ cm⁻³ M⁻¹ (assuming most metals have similar rates) concentration in the layer. Thus, if the HUNTEN et al., (1980) estimates of smoke and dust concentration at 90 km altitude are correct it seems plausible that the dust effects ion chemistry via at least electron attachment.

HUNTEN notes that the predicted dust content will Rayleigh scatter lidar signals much less than the atmosphere and thus not be detectable in this manner. However, there is some very preliminary evidence of charged dust (massive ions) effecting the incoherent scatter radar "ion line" spectrum.

MATHEWS (1984, 1986) describes incoherent scatter radar probing of the D region. In particular he describes the so-called ion line spectral shape as always being of Lorentzian shape for the collision dominated (diffusion limit) case and double humped for the wave limit. For the Arecibo 430 MHz radar the transition between the two regimes occurs between 90 km and 95 km altitude so that all D region spectra are in the diffusion limit. MATHEWS
also notes that the presence of negative ions broadens the spectrum in either limit as shown in Table 3 of that paper.

Figure 12 shows a sequence of Arecibo electron concentration profiles showing two different sporadic layers centered at 92 km and 112 km altitude. These layers are in every way normal when viewed in this manner and in Figure 13 the ion spectra of the lower layer are shown at one time (spectral and total power measurements are interleaved in time). The spectrum at 91.36 km is an example of the expected Lorentzian shape though its width is 13% narrower than the daytime molecular ion spectrum (TEPLEY and MATHEWS, 1985) because of the more massive metal ions characteristic of the layer. Most individual spectra are flat indicating no incoherent scatter signal.

Figure 14 shows that set of spectra measured next in sequence from those of Figure 13. Note that signal spectra occur only at the heights of those in Figure 13 but that the edges of the spectra are "turned up". These "events" are observed only occasionally but appear to be always associated with low lying sporadic layers and on the basis of Figure 13 to 14 like comparisons it seems certain that this phenomena is associated with the layer.

Use of a theoretical model of the incoherent scatter spectral shape indicates that these spectra are possible only in the transition region between the wave and diffusion spectral limits. Also and most importantly these spectra are consistent with 600-1000 amu ions having a negative ion-to-electron concentration ratio of about 3. These massive ions, if they exist, seem to occur only in horizontally small and vertically narrow "clouds" and do appear to be mixed (within the 600 m height resolution) with "normal" ions. Much more study remains concerning this possibly very important and just recognized phenomenon.

Again combined lidar and incoherent scatter radar studies of those layers might resolve the issue of massive versus "normal" ions. One straightforward indicator might be a dip in Ca⁺ content in a layer which exhibits the unusual incoherent scatter spectra.

IV. Summary and Discussion

We have attempted to show that meteoric debris in the ionosphere and upper middle atmosphere form an interesting, pervasive, and diagnostically useful subject for study. We suggest that metallic atomic ions which form as meteors "burn up" in the 80-110 km region circulate in the low and mid latitude region due to tidal and electrodynamic effects. The suggested circulation system includes an E to F to E region path with the equatorial fountain providing the only E to F region transport mechanism. Metal ions are returned to the E region via intermediate layers. High latitude upward transport mechanisms (eg. GREBOWSKY and PHARO, 1985) have not been discussed here. Also, not mentioned are the various aspects of the "sodium problem" which is amenable to lidar studies [eg. RICHTER et al., 1981; BATISTA et al., 1985 and references of both]. While the aeronomy of sodium parallels that of the pure metals there are apparent differences which demand a separate detailed treatment which cannot be undertaken here.
Fig. 12 Electron concentration profiles of a double layer sporadic E system at Arecibo. These profiles are unsmoothed in time or height and have 600 m height and 55 second time resolutions. The low lying layer has a peak concentration of $3 \times 10^4$ el/cc at 2121 hours and appears to perfectly "normal".
Fig. 13  A set of "normal" ion line spectra obtained between the 2112 and 2117 hrs profiles of Figure 12. The flat spectra indicate no signal while the Lorentzian shaped spectra correspond exactly in height to the lower sporadic layer in Figure 12.
Fig. 14 Similar to and immediately following the spectra shown in Figure 13. Note that the signal or sporadic E spectra have additional "wind" features. The features have been tentatively been identified with 600-1000 amu ions with a negative ion-to-electron concentration ratio of ~ 3.
We have also discussed some details of intermediate and sporadic E layer dynamics and chemistry. We demonstrate that intermediate layers have significant molecular ion makeup and that metallic ions suppress molecular ion concentration in both intermediate and sporadic E layers. We note that no satisfactory explanation for intense (blanketing) sporadic E exists.

Also discussed are aspects of metal ion chemistry in the 90 km altitude "dumping" region. Included here is the role of these ions in the formation and growth of dust. If the HUNTEN et al., (1980) estimate of dust or smoke surface area is correct then this form of meteoric debris quite likely effects the ion chemistry of the region. The Arecibo incoherent scatter radar has possibly detected the massive (600-1000 amu) ions involved in this interaction.

We conclude that study of meteoric debris particularly in the 80-120 km region is vital to understanding at least the ion chemistry of the region. This study would also lead to much new information concerning the formation, growth, and effects of dust in the region. Common volume, simultaneous lidar and incoherent scatter radar measurements particularly if supplemented with rocket measurements of the D and E regions would yield the best data concerning these issues.

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