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THE INCREASED ATTACHMENT DUE TO IONIZATION-INDUCED SMOG IN EMP ENVIRONMENTS

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The increased electron attachment due to HNO_2 production in the EMP source region is investigated. The HNO_2 produced is found to be roughly linear with the total ionization up to an ionization value of about 2×10^{10} ion pairs. Above this, the HNO_2 production is less than linear. Although the attachment to HNO_2 was not enough to explain the lightning strokes in the Mike shot, it can affect the fields in the EMP source region. The attachment to other species via endothermic reactions which involve electrons which		

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20. ABSTRACT (Continued)

have been heated by the electric field was also investigated. It was concluded that only those reactions in which the energy change is small, such as the reactions with O_3 , HNO_2 , and H_2O_2 , hold much hope of contributing significantly to the overall attachment. The necessary experimental data for these reactions, however, is not available.

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INTRODUCTION

The reliability of EMP calculations depends on having accurate values for the electron and ion (both positive and negative) concentrations and for the mobilities of these charged particles. The electrical conductivity of air, which is a strong limiter of the fields produced, is proportional to the sum, over charged particle species, of the product of particle density and mobility.

The production of ionization by the gamma rays is easy to calculate as are the ratios of the simple positive ion species initially formed. The subsequent ion transformations and the electron and ion decay schemes are not so well known.

Until now, the calculations of the ion and electron densities for system purposes has been accomplished by the use of a very simple model involving only one positive ion species, n_+ , and one negative ion species, n_- , in addition to the electron density, n_e . This model can be described by the following equations:

$$\frac{dn_e}{dt} = q - \alpha_d n + n_e - A n_e + D n_- , \quad (1)$$

$$\frac{dn_+}{dt} = q - \alpha_d n_e - \alpha_i n_- n_+ , \quad (2)$$

$$\frac{dn_-}{dt} = A n_e - D n_- - \alpha_i n_- n_+ , \quad (3)$$

where q is the ion pair production rate, α_d is the effective electron-ion recombination (usually dissociative) coefficient, α_i is the effective ion-ion recombination coefficient, D is the effective detachment coefficient, and A is the effective electron attachment coefficient. At sea level, the detachment of electrons from negative ions is usually

negligible, except in a small volume of air very near the nuclear fireball where the radiation flux or kinetic temperature is very high, and this term is usually omitted.

The above model constitutes an enormous simplification. The actual deionization process in air can involve 50 or more ion species and almost as many neutral species, most of which are created by the deposition of energy and subsequent chemical interactions. This complexity is gathered into the effective coefficients which are usually chosen to be dependent only on temperature. In reality, they are also functions of altitude, ambient air species concentration, ionization rate and time.

For low altitudes (<30 km) and times greater than about 10^{-3} seconds, however, the electron density depends only on the ionization rate, q , and the attachment coefficient, A . Since the electron density rapidly falls much below the ion densities, the positive and negative ion densities, after a short time, are approximately equal and depend only on q and the coefficient α_i . The value of α_i is dependent on the identity of the ions involved but very little is known as to the ion identities at sea level and the individual values of α_i for these ions. The value of the effective α_i is thus usually taken to be the same for all ion combinations and there is some evidence that this is a reasonable assumption.

The attachment coefficient is, generally, the simplest of the effective rate coefficients. It can usually be associated with the three body attachment of electrons to molecular oxygen, i.e.,



where M is O_2 , N_2 or H_2O . At sea level and ambient temperature, the value of the effective attachment coefficient derived from reaction 4 is about 10^8 sec^{-1} .

There has been some reason, from observational data, to suspect that the simple air chemistry model used in EMP calculations is inadequate. We refer here to the "lightning" strokes seen in the Mike shot¹ (Figure 1) and other large yield shots. The fact that these strokes are oriented along arcs of circles centered on the burst point is convincing proof that they are driven by the EMP electric field. However, the calculated EMP fields are not large enough for these strokes to occur. One possible conclusion is that the calculated air conductivity is too high, by a factor of about four or five, in the time frame of about 0.1 to 10 milliseconds, when the lightning occurs. According to the calculations, the conductivity is primarily due to the electrons and not the ions. Given a fixed ionization rate, the only way to reduce the conductivity is to reduce the electron density; and, in the time regime in which we are operating, the only way to do this is to increase the attachment rate.

The rate coefficient of the attachment to O_2 indicated by reaction 4 is fairly well established, and its uncertainty cannot account for the factor needed to lower the electron density the amount required to explain the lightning strokes.

It is known that the chemistry following the deposition of ionizing radiation leads to the copious production of many atomic and molecular species (called smog in the trade) which are not ordinarily present in air in significant quantities. The molecular species formed include NO , NO_2 , O_3 , HO_2 , H_2O_2 , HNO_2 , and HNO_3 . NO_2 and O_3 can attach electrons with two body rate coefficients of the order of 10^{-11} cm^3/sec . This is, however, not large enough to compete with reaction 4 when even the maximum amounts of NO_2 and O_3 which can be formed are considered. Recently, however, a rate coefficient of 5×10^{-8} cm^3/sec . at 300K has been measured² for the attachment reaction



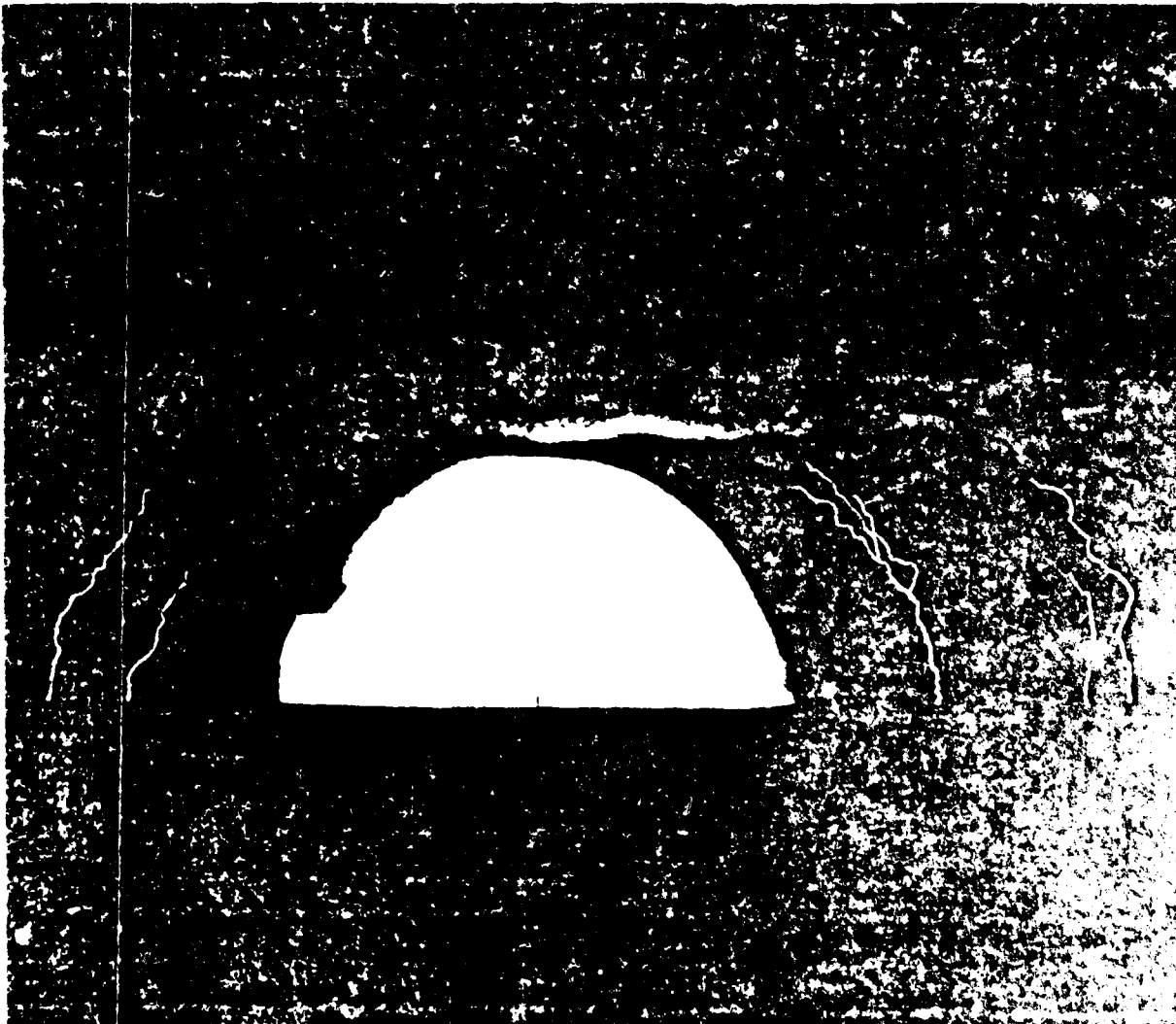


Figure 1. Lightning induced by a surface thermonuclear explosion in the Pacific. The five lightning channels have been inked for better reproduction.

For this reaction to compete with reaction 4 requires a concentration of HNO_3 of at least $2 \times 10^{15} \text{ cm}^{-3}$. As we shall see later, the amount of HNO_3 production is about 0.25 of Q , the total number of ion-pairs formed by the energy deposition ($Q = \int q dt$), when Q is less than or equal to 10^{16} cm^{-3} . Thus, if we have a Q equal to or greater than $8 \times 10^{15} \text{ cm}^{-3}$, the HNO_3 could contribute significantly to the electron attachment.

The first calculation was done using a total ionization of $7 \times 10^{16} \text{ cm}^{-3}$. This was based on use of gamma source and transport formulae for normal bombs, scaled to the Mike neutron yield. At this high value, the production of HNO_3 was only about 0.1 of Q but this was enough so that HNO_3 strongly dominated the electron attachment and yielded an electron density much below the value calculated using the usual model.

It was pointed out to us by Dr. Forrest Gilmore, however, that this value of Q was much too high for the Mike burst. Measurements taken during that particular shot show an anomalously low dose rate at 2300 meters³. Scaling this data³ yields roughly a Q at 10^{-2} sec . and 500 meters from the burst of $2 \times 10^{16} \text{ cm}^{-3}$. At 1000 meters, which is more representative of the distances of the lightning strokes, the value of Q would be about 10^{15} cm^{-3} . Thus, at this time, the attachment to HNO_3 is at least an order of magnitude too small to explain the lightning strokes observed during the Mike shot³.

Other mechanisms exist which may explain the lightning strokes. One possibility is that leader growth is enhanced because of substantial background ionization and negative ion detachment mechanisms. Another possibility is introduced by the fact that, due to the electron fields, the electrons in the EMP source region can be much more energetic than the atoms or molecules. Endothermic attachment reactions which are insignificant at ambient temperatures may become important at the elevated electron temperatures.

Even though the HNO_3 production has not provided an explanation for the lightning strokes, it can impact the electron density, conductivity and electric field distribution in the EMP source region and therefore deserves some further study. In the next section, we describe the calculations already made and the chemistry involved in the HNO_3 production. The following section deals with the possibility of the enhancement of attachment by hot electrons. The last section deals with our conclusions.

THE PRODUCTION OF HNO_3 IN THE EMP SOURCE REGION

The formation of HNO_3 is accomplished mainly by the reaction



Although this is a three body reaction, at sea level density, the reaction has begun to saturate and behaves more as a two body process⁴. The rate coefficient used in these calculations for reaction 6 was

$$k_6 = 1.1 \times 10^{-11} \left(\frac{300}{T} \right)^{1/2} \text{ cm}^3/\text{sec} . \quad (7)$$

The NO_2 available to form HNO_3 is formed from the atomic nitrogen which is produced by the initial energy deposition. About 1.2 nitrogen atoms are formed per ion pair. Some of this is in the form of N^+ but the bulk is in the form of neutral nitrogen in the ground state, $\text{N}(^4\text{S})$, and is the first excited state, $\text{N}(^2\text{D})$. Figure 2 is a schematic of the chemistry scheme used for the "odd nitrogen." The $\text{N}(^4\text{S})$ and $\text{N}(^2\text{D})$ are the starting points, and the heavy arrow indicates major reaction paths. The dotted arrows indicate reaction paths for which the reaction rates and products are uncertain or unknown and where strong assumptions were made. The species shown along the connecting arrows are the reactants involved in the various reaction paths.

We see that the atomic nitrogen can react to form NO , N_2O , or N_2 . The reactions forming N_2 and N_2O involve the reaction of atomic nitrogen and NO , NO_2 or N . If the total ionization is small and/or spread out over an extended period of time, these species concentrations are never very large simultaneously and the reformation of N_2 is minimal. When the total ionization is large, N_2 reformation is significant and there is less NO and NO_2 available to form HNO_3 and HNO_2 (which competes with HNO_3 for the available odd nitrogen). This is why the efficiency of HNO_3 production is decreased when the total ionization in our calculations is large ($>10^{16} \text{ cm}^{-3}$).

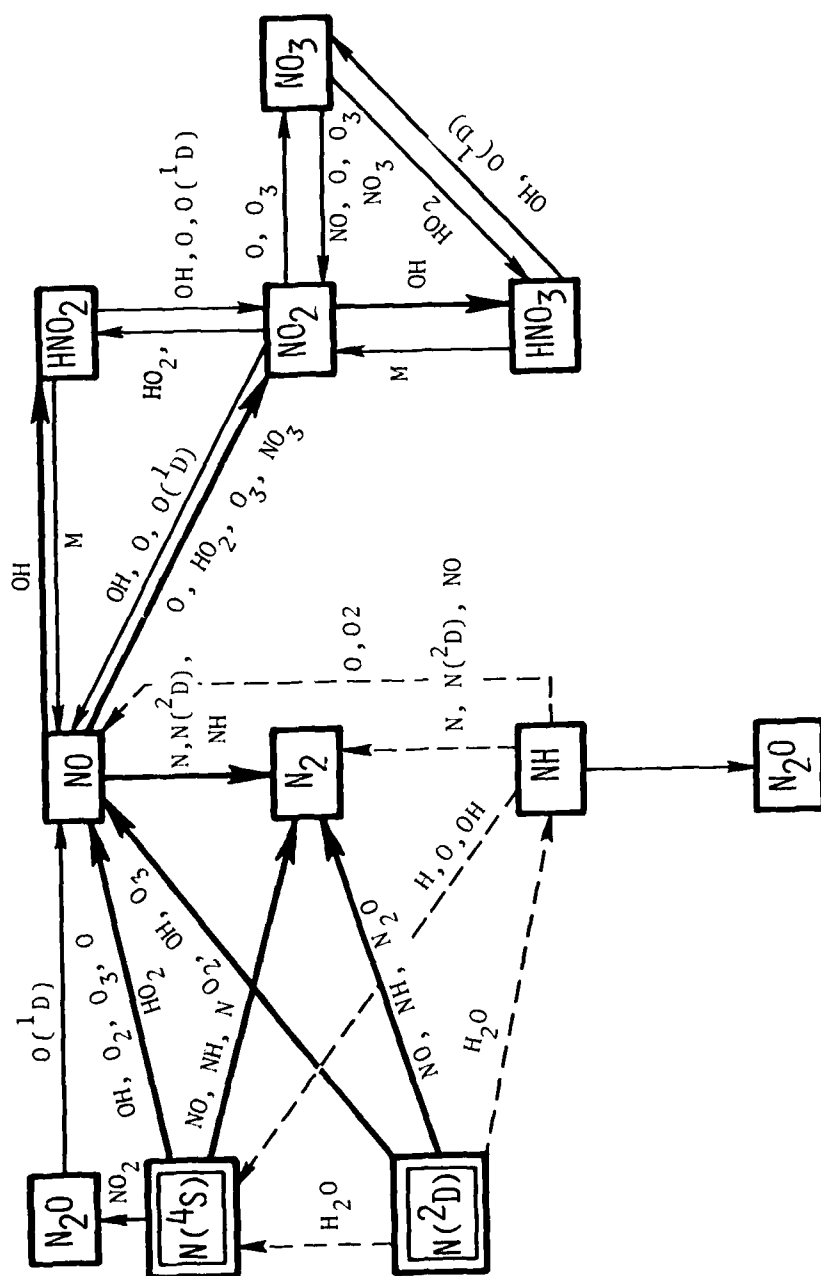


Figure 2. Odd nitrogen reaction scheme.

The critical reactions in this scheme are the formation of N_2 and NO from the atomic nitrogen, the oxidation of NO to NO_2 , in our case primarily by HO_2 , and the formation of HNO_2 and HNO_3 from NO and NO_2 by association with OH. The rate coefficients for these reactions are fairly well known. The role of NH, however, is uncertain. At sea level, virtually all the $N(^2D)$ formed is quenched by H_2O . The products have not been identified but probably are NH and OH. NH is known to react with NO with a rate constant of about $4 \times 10^{-11} \text{ cm}^3/\text{sec}$, but its reactions with N, O, H, OH and O_2 are unknown. With the exception of the reaction of NH with O_2 , we have assumed rate coefficients of the same order as the reaction with NO. The rate coefficient for the reaction with O_2 was assumed to be about a factor of 5000 smaller at 300K. These reactions and coefficients constitute the greatest uncertainty in the odd nitrogen reaction scheme and variations within the large area of uncertainty could significantly affect the eventual HNO_3 production.

Some of the H, OH, and HO_2 , or "odd hydrogen," is formed in the reactions of $N(^2D)$ and $O(^1D)$ (formed by the initial deposition of energy) with H_2O , and in the reactions of NH. The bulk, however, is formed in the process of positive ion hydration.

The ions formed initially are N^+ , O^+ , N_2^+ and O_2^+ . Prior to recombination, however, almost all of these ions are transformed into a series of more complex ions terminating with the hydronium ion H_3O^+ . $(H_2O)_n$, where n can be very large. Figure 3 shows one of the schemes by which this occurs. Much of the N^+ , O^+ and N_2^+ reacts with various neutral species to form O_2^+ . The O_2^+ either directly or indirectly clusters to form $O_2^+ \cdot H_2O$, which then reacts with H_2O to form the hydronium cluster. There are other schemes, particularly one involving NO^+ , which lead to the hydronium ion, but the one shown is the most important under strongly disturbed condition.

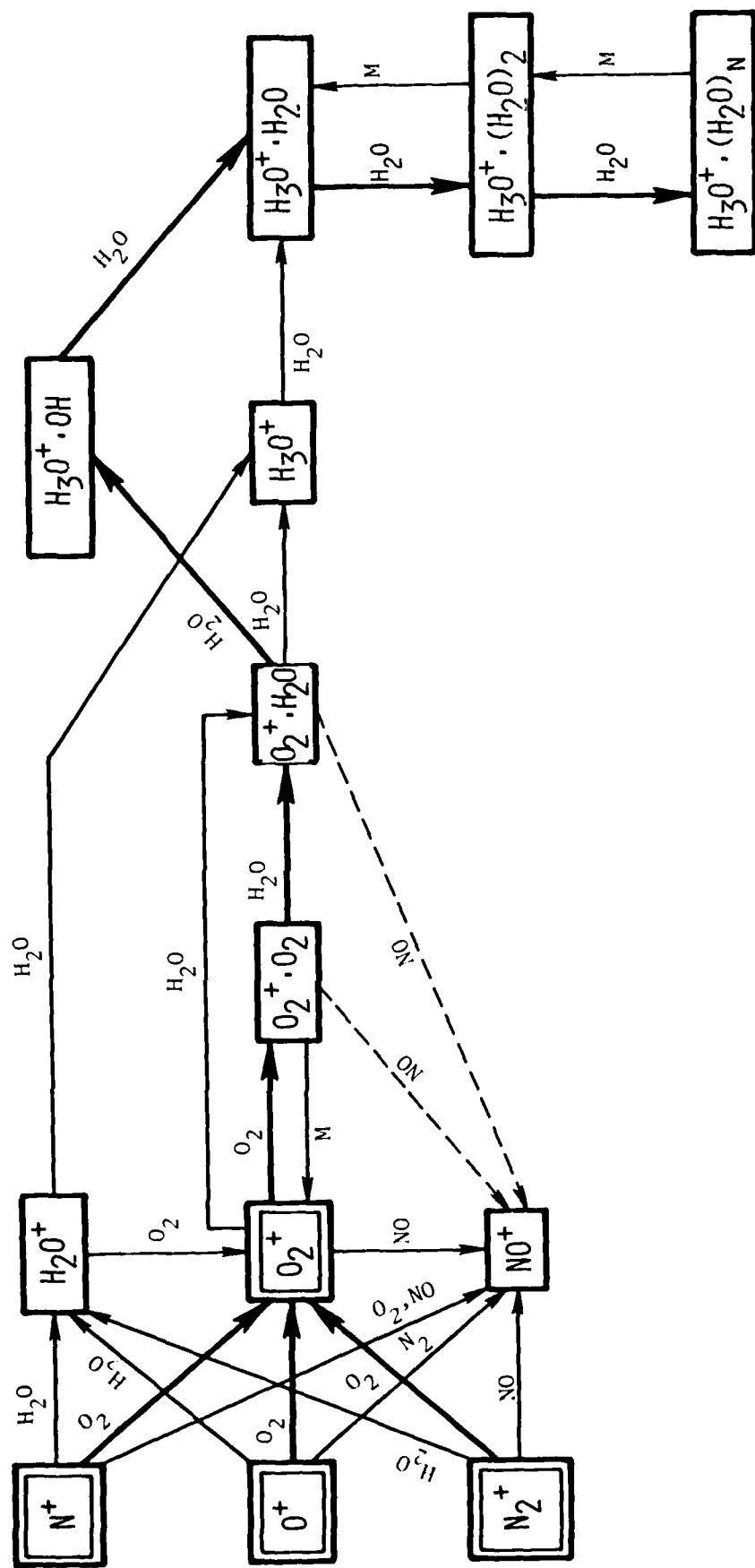


Figure 3. Formation of hydronium ions via O_2^+ .

It is obvious that, in the transformation of any of the initial ions to a cluster of H_3O^+ , an OH molecule is released. When the H_3O^+ cluster recombines, either with an electron or a negative ion, another odd hydrogen species is released. This is the major source of odd hydrogen in our problem. In the recombination of $\text{H}_3\text{O}^+ \cdot (\text{H}_2\text{O})_n$ we have assumed that a free hydrogen atom is released, the fate of which, almost always, is to associate with an O_2 molecule to form HO_2 . When recombining with negative ions, this may not be true. Species such as OH, HO_2 , HNO_2 and HNO_3 may be formed, depending on the negative ion, as a direct result of the charge neutralization process. The significance of this upon our problem has not yet been investigated.

Figure 4 is a schematic of the odd hydrogen chemistry scheme. The most critical reaction in this scheme is the reaction between OH and HO_2 to form H_2O and O_2 . This reaction is the main process by which the total odd hydrogen is depleted and H_2O reconstituted. The rate coefficient used in the calculations for this reaction was $2 \times 10^{-11} \text{ cm}^3/\text{sec}$. A larger rate coefficient is now being recommended⁴ ($4 \times 10^{-11} \text{ cm}^3/\text{sec}$). Increasing this rate coefficient will decrease the OH that is available to associate with NO_2 and thus could decrease the total HNO_3 production. Another area of uncertainty has already been mentioned in the last paragraph and concerns the fate of the hydrogen atom made available by the neutralization of the H_3O^+ cluster with various negative ions.

Figures 5 and 6 show the species concentrations as a function of time for a total ionization, Q , of 10^{16} ion pairs/ cm^3 . The specific ionization function used was

$$q = 10^{20} e^{-10^4 t} \text{ ion pairs/cm}^3. \quad (8)$$

This function essentially "turns off" by 10^{-3} second. The time is measured from the arrival of the radiation at the point in question.

Figure 5 shows the odd hydrogen species plus H_2 and O_3 . Figure 6 shows the odd nitrogen species plus N_2O . We see that the important species OH and HO_2 rise rapidly to a maximum of about 10^{15} cm^{-3} as the ion hydration and recombination produces H and OH and the H associates with O_2 to form HO_2 . After a time of about 5×10^{-5} seconds, the ionization rate decreases significantly, and the reaction between OH and HO_2 to form H_2O and O_2 has an appreciable effect, causing the OH and HO_2 to decrease. Though these are the main determinants of the OH and HO_2 behavior, other reactions are appreciable, in particular, the reactions of OH or HO_2 with $N(^4S)$, O , NO and NO_2 . The first rise of the atomic hydrogen is due to its production by clustered hydronium ion recombination. The second rise is due to reactions of $N(^4S)$ and O with OH which adds to the production of H . The decrease of H after 5×10^{-5} seconds is predominantly due to the decrease of the ionization rate and the association of H with O_2 to form HO_2 . Hydrogen peroxide, H_2O_2 , is formed primarily by the association of two OH molecules. It reaches a value of about $2 \times 10^{15} \text{ cm}^{-3}$ at 2×10^{-4} seconds and remains approximately constant beyond that because of the decay of the OH . The ozone O_3 is shown because it is a significant oxidizer of NO and may play a role in electron attachment at high electron temperatures. It is formed primarily by association of O_2 with atomic oxygen. The slight decay after 10^{-3} seconds is due to its breakup by $O_2(^1\Delta)$, a long lived metastable state of oxygen produced by the energy deposition. Also shown in Figure 5 is H_2 which is formed by the reactions of H with HO_2 , NH and H_2O_2 .

The NO in Figure 6 is formed mainly by the reactions of $N(^2D)$ and NH with O_2 and the reactions of $N(^4S)$ with OH , O_2 and HO_2 . The decline after 10^{-4} seconds is due to those reactions which oxidize NO to NO_2 , or which form HNO_2 . The NO_2 rises rapidly after 10^{-6} seconds and levels off at a value of about $3 \times 10^{15} \text{ cm}^{-3}$ when the production of odd nitrogen ceases and the NO concentration drops. The behavior of the

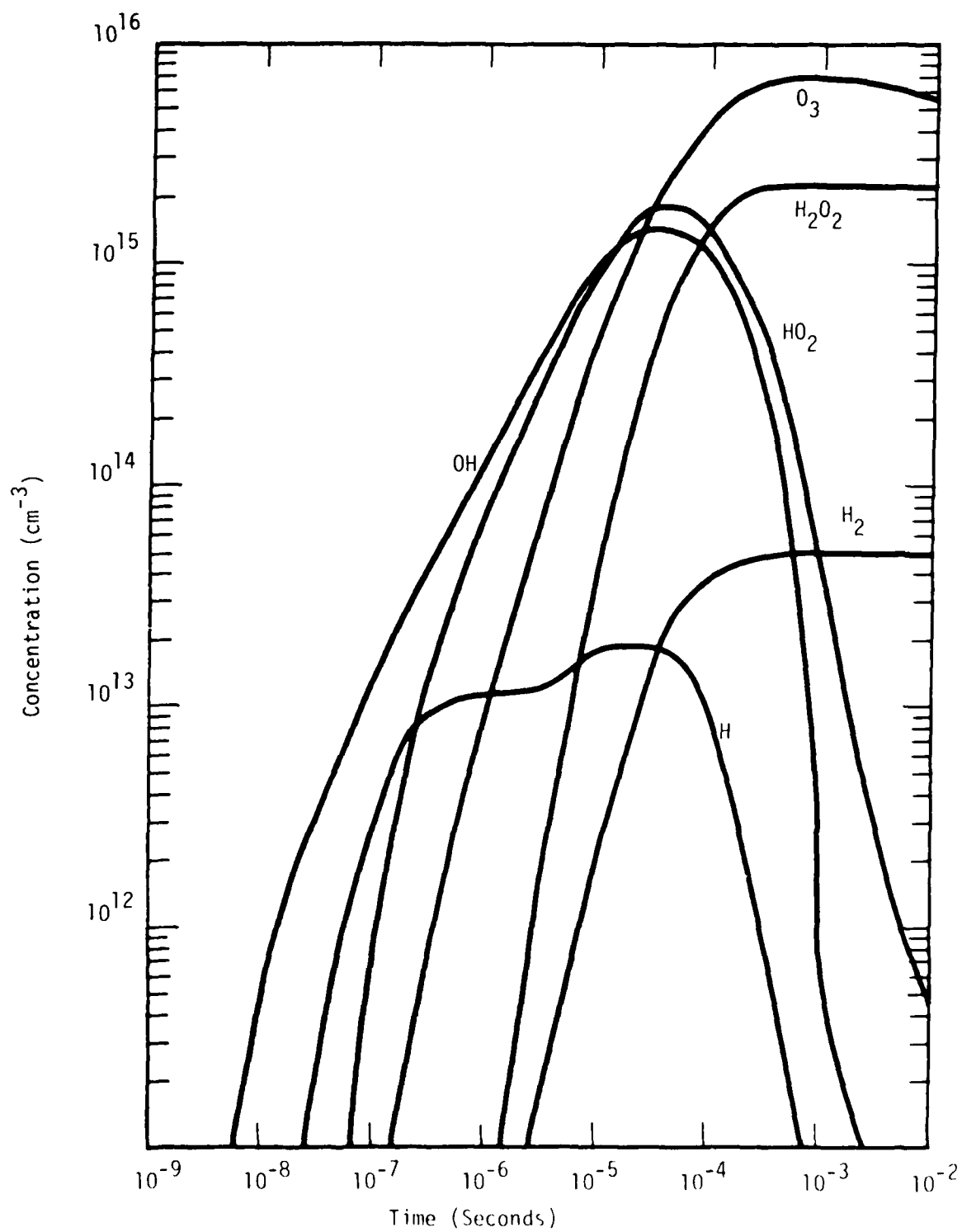


Figure 5. Odd hydrogen, H₂ and O₃ species concentrations.

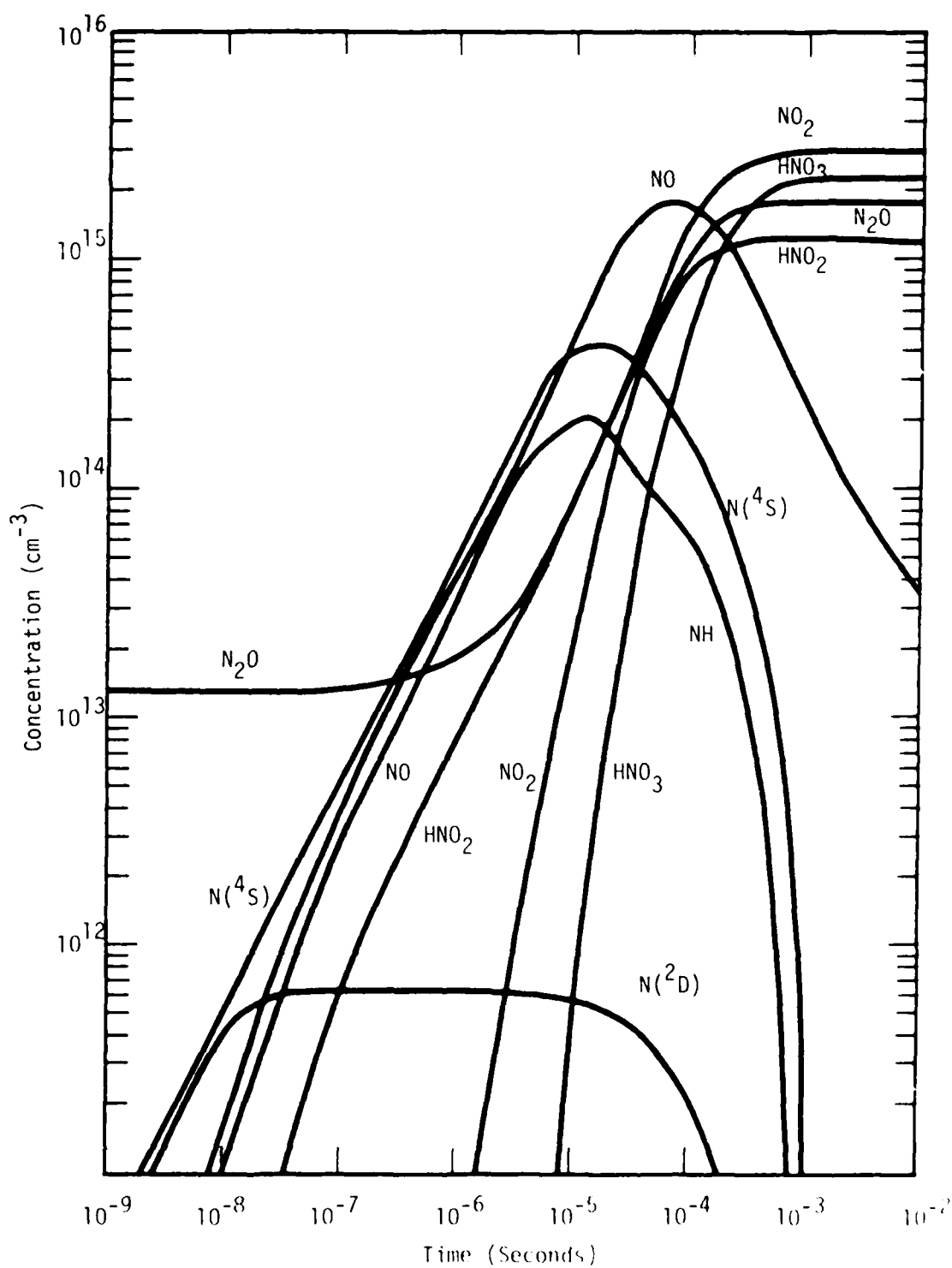


Figure 6. Odd nitrogen and N₂O species concentrations.

HNO_3 is similar to that of the NO_2 , from which it is formed. The leveling off at about $2.4 \times 10^{15} \text{ cm}^{-3}$ slightly before 10^{-3} seconds is due to the disappearance of the OH which is necessary for HNO_3 formation. The behavior of HNO_2 is very similar to that of HNO_3 except that significant quantities are formed earlier because of the presence of NO at these times. Figure 6 also shows the N_2O concentration which increases from an ambient value of $1.3 \times 10^{13} \text{ cm}^{-3}$ to a value of almost 2×10^{15} after 3×10^{-5} seconds. The N_2O is almost all produced by the reaction of $\text{N}(^4\text{S})$ with NO_2 and therefore ceases when the $\text{N}(^4\text{S})$ concentration becomes small.

This calculation was made using a water vapor concentration of 1 percent. Other calculations were made with this same water vapor concentration for different values of the total ionization from 10^{15} cm^{-3} to $7 \times 10^{16} \text{ cm}^{-3}$. As indicated in the introduction, below a value of about $2 \times 10^{16} \text{ cm}^{-3}$, the HNO_3 production is about 0.25 per ion pair. Above $2 \times 10^{16} \text{ cm}^{-3}$, the reactions reconstituting N_2 from the odd nitrogen species become important and the efficiency of HNO_3 production drops. At $7 \times 10^{16} \text{ cm}^{-3}$ total ionization, it is about 0.1 per ion pair.

A set of calculations were also made with a water vapor concentration of 1 percent. These showed very little difference in the HNO_3 concentrations with the 1 percent calculations. The basic reason for this is that at both water vapor concentrations virtually all of the ions formed transform to the hyronium clusters before recombination and virtually all of the $\text{N}(^2\text{D})$ reacts with H_2O rather than with O_2 . The water vapor concentration would have to be decreased to below 0.1 percent before any significant differences occur. At the lower water vapor concentrations, however, the attachment due to reaction 4 (attachment to O_2) when H_2O is the third body is decreased. Thus, since the HNO_3 concentrations are the same, the relative contribution of HNO_3 to the electron attachment is greater when the water vapor concentration is small.

At an integrated ionization value of 10^{16} cm^{-3} , we had a value for the HNO_3 concentration of $2.4 \times 10^{15} \text{ cm}^{-3}$ at 10^{-3} seconds. This yields a contribution to the attachment of $1.2 \times 10^8 \text{ sec}^{-1}$. The contribution from O_2 attachment when the H_2O relative concentration is 2 percent and the temperature is 350K (the energy deposited raises the temperature in this case about 55K) is $1.1 \times 10^8 \text{ sec}^{-1}$. Thus, the HNO_3 doubles the attachment and halves the electron density at this time. This is not enough to explain the lightning strokes in the Mike shot but is enough to cause significant effects in the EMP phenomena. At 500 km distance from the Mike burst, we had a Q of $2 \times 10^{16} \text{ cm}^{-3}$ at 10^{-2} seconds. This would give us an attachment rate a factor of three larger than is currently predicted.

The uncertainties involved in the NH reaction scheme and the ion-ion recombination have already been mentioned. Another possibly important uncertainty involves the role of photodissociation by bomblight. This not only applies to the photodissociation of HNO_3 but also to species such as NO_2 , HO_2 and O_3 . The photodestruction of NO_2 and HO_2 would interrupt the chain of reactions leading to the formation of HNO_3 . The photodissociation of O_3 would lead to a large atomic oxygen population at the times of interest. This atomic oxygen would react with HO_2 and NO_2 and further tend to deplete these species. Rough calculations indicate that at a kilometer distance photodissociation probably does not play a significant role. At 500 meters, however, it may have a significant effect. This and the other uncertainties should be investigated.

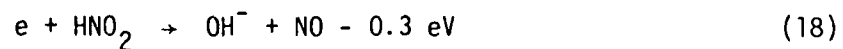
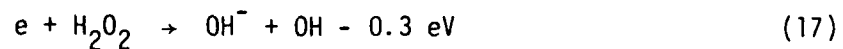
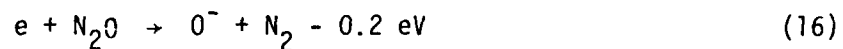
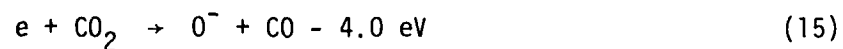
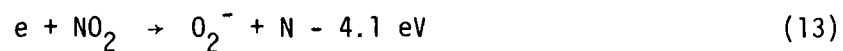
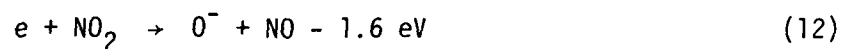
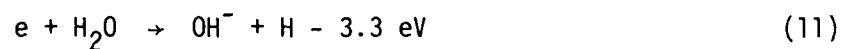
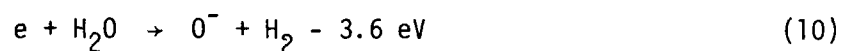
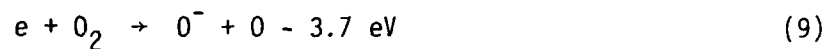
INCREASED ATTACHMENT DUE TO HOT ELECTRONS

Another possible source of increased attachment stems from the fact that in the EMP source region the electric fields which are generated are capable of heating the electrons to temperatures considerably above the ambient heavy particle temperature. Electron temperatures (the velocity distribution is not, strictly speaking, Maxwellian, but, except for the high energy tail, this is a fairly good assumption) of up to 1 eV are attainable and this opens up the possibility that a number of endothermic dissociative attachment reactions which are not significant at ambient temperatures may become so. A list of a number of these possibilities is shown in Table 1. Shown also are the energy changes involved in the reactions.

The reactions in Table 1 were chosen because the neutral reactants are either present in the ambient atmosphere in large amounts (O_2 , H_2O , and CO_2) or are produced copiously by the energy deposition and do not decay quickly after the ionization source is turned off, at least not in the time scale of less than a second. The rate coefficients of the reverse of reactions 9 to 15 have been measured, at least at room temperature, and this enables us to obtain rate coefficients for the forward reactions by detailed balancing. This, however, is done assuming that the reactants and products have Maxwellian velocity distributions and Boltzmann distributions in internal energy states. If the neutral species formed by the reverse of the reactions in Table 1 are preferentially produced in highly excited states, detailed balance will overestimate the rate coefficients of the forward reactions. What information that exists on the forward reactions indicates that this is the case, at least for some of the reactions.

The reactions 9 to 15 all have rate coefficients for the associative detachment reverse reactions between $1.5 \times 10^{-10} \text{ cm}^3/\text{sec}$ and $1.4 \times 10^{-9} \text{ cm}^3/\text{sec}$ at 300K^5 . Little is known about the temperature

Table 1. Endothermic dissociative attachment reactions



dependence of these rate coefficients. The rate coefficients of the forward dissociative attachment reactions, k_a , can be obtained from the reverse detachment rate coefficients, k_d , by the relation

$$k_a = k_d K_{eq} \left(\frac{T}{T_e} \right)^{2.5} \quad (19)$$

where T_e and T are the electron and molecular temperatures, K_{eq} is the equilibrium constant assuming all temperatures are equal, and the term in parentheses takes into account that T_e and T may be considerably different.

Of the reactions in Table 1, more experimental data is available for reaction 9 than any of the others. Use of equation 19 yields

$$k_9 = 3.4 \times 10^{-5} \left(\frac{300}{T} \right) \left(\frac{T}{T_e} \right)^{2.5} e^{-42400/T_e} \quad (20)$$

Taking $T = 300K$ and $T_e = 6000K$ and $12000K$, we obtain values of k_9 of 2×10^{-11} and $10^{-10} \text{ cm}^3/\text{sec}$, respectively. This yields attachment rates of 10^8 and $5 \times 10^8 \text{ sec}^{-1}$, respectively, at sea level. The fact that the electron densities in the high energy tail of the velocity distribution are probably significantly larger than Maxwellian densities would further increase the attachment rates. The experimental data, however, does not support these values. The cross section data for reaction 9, for different O_2 temperatures and as a function of electron energies, are shown in Figure 7⁶. Using the curve for $T = 300K$, we obtain a value of k_9 of roughly $4 \times 10^{-14} \text{ cm}^3/\text{sec}$ for $T_e = 6000K$ and 4×10^{-14} for $T_e = 12000K$. This is considerably less than obtained by detailed balance and almost certainly indicates that in the dissociative attachment of O^- by O (the reverse of reaction 9) the O_2 is produced in vibrationally excited states. This would explain the significantly increased cross sections in

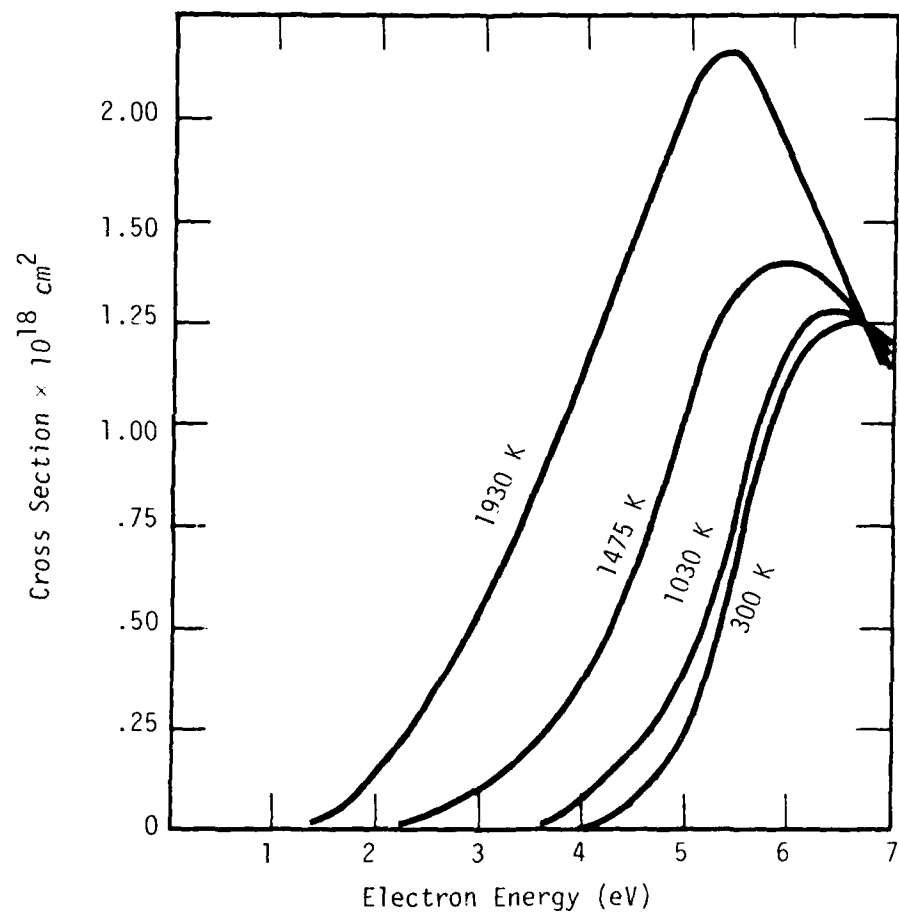


Figure 7. Cross sections for associative detachment to O_2 .⁶

Figure 7 when the O_2 temperature is increased. When the O_2 temperature is 1930K, we obtain values of k_9 of $4 \times 10^{-12} \text{ cm}^3/\text{sec}$ for $T_e = 6000\text{K}$ and $3 \times 10^{-11} \text{ cm}^3/\text{sec}$ for $T_e = 12000\text{K}$. We see that we are getting into the O_2 temperature region in which dissociative attachment to O_2 may contribute significantly to the overall attachment.

The potential contribution of reaction 9 to the attachment depends, therefore, on whether a significant amount of vibrational excitation can be maintained over a period of time of up to one or more milliseconds. The rapid deactivation of vibration excited O_2 by H_2O ($1.7 \times 10^{-11} \text{ cm}^3/\text{sec}$)⁶ makes this highly unlikely. Mechanisms such as vibration transfer from excited N_2 , or chemical reactions such as $O + O_3 \rightarrow O_2(^1\Delta) + O_2^{\ddagger}$, or excitation by electrons and ions accelerated by the electric field are not rapid enough to maintain the necessary amount of O_2 vibrational excitation against this large a deactivation rate.

The situation is similar for other reactions for which there are cross section data. The cross section data for dissociative attachment to CO_2 at 300K⁷ also yield a rate coefficient much less than that predicted by detailed balance. For N_2O , however, the cross section data⁷ yield values of k_{16} which, though small, are not greatly different than those one would expect from detailed balancing. One can hypothesize that this is due to the fact that the energy needed to make this reaction go is only 0.2 eV rather than the 3.7 and 4.0 eV needed for the reactions with O_2 and CO_2 (see Table 1). In a dissociative detachment reaction which is resonant using ground state energies, excited products will not likely be produced and one would then expect detailed balance to yield the correct rate coefficient for the attachment reaction. One could assume, therefore, that the closer the reaction is to resonance the more reliability one can place on detailed balance. This reasoning would seem to indicate that the last three reactions in Table 1 and reaction 14 would be the most promising. With only a little vibrational excitation and a moderate

electron temperature of a few tenths of an electron volt, these reactions might contribute significantly to the attachment rate.

There is no information concerning reactions 17 and 18, but the rate coefficient of the reverse of reaction 14 has been measured to be $1.5 \times 10^{-10} \text{ cm}^3/\text{sec}$ at 300K. By detailed balance, we obtain

$$k_{14} = 1.6 \times 10^{-4} \left(\frac{300}{T} \right) \left(\frac{T}{T_e} \right)^{5/2} \quad (21)$$

For $T = 300\text{K}$ and $T_e = 3000\text{K}$ we have $k_{14} = 5 \times 10^{-8}$. If we assume a value of one ozone molecule formed per ion pair produced (a reasonable value for Q between 10^{15} and 10^{16} cm^{-3}), we would have the attachment to O_3 equal to 10^8 sec^{-1} for $Q = 2 \times 10^{15} \text{ cm}^{-3}$. This is the Q we would expect about 900 meters from the Mike burst.

Again we must know whether vibrational excitation is involved and, if so, whether sufficient vibrational excitation can be maintained under our conditions. No information is available on whether O_3 is produced in a vibrationally excited state in the associative detachment of O_2^- by atomic oxygen, but it would be reasonable to assume that it is. Because the endothermicity is only 0.6 eV, however, we would not expect that vibrational excitation will be as important as in reaction 9. In addition, there is a possibility that an O_3 vibrational state distribution with a temperature higher than ambient can be maintained over much of the time of interest. The quenching rate coefficient of O_3^+ by N_2 and O_2 is about $2 \times 10^{-14} \text{ cm}^3/\text{sec}$ ⁸. The process which forms ozone, the three body association of atomic oxygen with O_2 , has a rate coefficient of about $7 \times 10^{-34} \text{ cm}^6/\text{sec}$ and also forms it with about five quanta of vibrational energy⁸. Once a steady state is attained, the amount of O_3^+ will be roughly equal to the atomic oxygen concentration. Thus, as long as the atomic concentration is a significant fraction of the O_3 concentration, the O_3 will be significantly excited.

The measurements made during the Mike shot can be interpreted as indicating that the prompt pulse of ionizing radiation lasts more like 10^{-2} second rather than the 10^{-3} second we have assumed in our calculations. This would extend in time the production of atomic oxygen and result possibly in a significant ozone excitation out to times of the order of milliseconds.

The attachment to H_2O_2 and HNO_2 involves about half the amount of energy difference than the attachment to O_3 and therefore should be even less sensitive to the need for vibrational excitation. Attachment cross section information is needed for these species and O_3 , preferably as a function of both electron energy and molecular temperature.

CONCLUSIONS

Though the attachment to HNO_3 cannot, at this point, explain the lightning strokes observed during the Mike shot, it nevertheless may play a role in determining the electron density and conductivity in the EMP source region. From the calculations made to date, the efficiency of HNO_3 production is about 0.25 per ion pair for total ionization levels below about $2 \times 10^{16} \text{ cm}^{-3}$. The contribution to the effective attachment coefficient is given by

$$\Lambda_{\text{HNO}_2} \approx 10^{-8} Q \text{ sec}^{-1} \quad (22)$$

A more careful study of the uncertainties involved may change this number. In particular, the effect of photodissociation by bomb light may decrease this number appreciably at distances close to the burst point.

The possibility exists that the total electron attachment may also be augmented significantly by dissociative attachment reactions which are endothermic. This is brought about by the fact that the electric field generated within the EMP source region heats the free electrons to temperatures appreciably higher than ambient temperature. The data which exist indicate, however, that the attachment rate coefficient is highly sensitive to the degree of vibration excitation in the molecule, particularly if the energy difference is large. This would seem to rule out species such as O_2 , H_2O and CO_2 as good attachers in our case. The strong possibility exists that when the energy difference is small, such as with O_3 , H_2O_2 and HNO_2 , the rate coefficient is not critically dependent on the vibrational excitation of the molecule. This is particularly true of H_2O_2 and HNO_2 , but nothing is known about these attachment rates.

Some further investigation is needed regarding HNO_3 production in the EMP source region. The effect of the uncertainties associated with the NH reactions and ion-ion recombination products should be studied as well as the effect of photodissociation by bomb light.

In the area of associative attachment, a study should be made to determine the specific electron velocity distributions in air brought about by different electric field strengths. The effect of collisions with the species produced by the radiation should be included. Particular attention should be placed on the high energy tail of the distribution. With this information available, a quantitative evaluation is possible to determine what cross sections are needed for various species to make them important in the attachment process. If these cross sections are reasonable, recommendations for experimental studies can be made.

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