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Spacecraft Interaction with Atmospheric Species in Low Earth Orbit

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Spacecraft interaction with ambient atmospheric species (O, N_2, O^+, and electrons) in low Earth orbit involves collisions at high energies, giving rise to such complex phenomena as the shuttle glow, plume-atmosphere interactions, and plasma modifications. A survey of these and other effects is presented, and conclusions are drawn about possible ambiguities in interpretation of present data. For example, a suggestion is made that ions may play a role in the Shuttle glow phenomenon. Lack of data on the accommodation (in terms of energy and in terms of adsorption and subsequent reactions) of atmospheric species, such as O and N_2, on amorphous surfaces at hyperthermal energies is a distinct handicap in the development of appropriate numerical codes for predicting the effects of spacecraft interactions.

Introduction

THE atmosphere in low Earth orbit (LEO, 200–700-km attitude) consists primarily of neutral O and N_2 and of O^+ and electrons. At an altitude of 300 km the densities of the atmospheric constituents are[1] $[O] \sim 10^8$ cm^{-3}, $[N_2] \sim 2 \times 10^7$ cm^{-3}, $[O^+] \sim [e] \sim 10^5$ cm^{-3}. Although the neutral density is considerably greater than the plasma density, it should be kept in mind that ion–neutral reactions have rate coefficients that are 100–1000 times greater than neutral–neutral reactions. Thus, under some circumstances ion–neutral reactions may become as important as the neutral–neutral reactions. Likewise, ion–surface reactions may play an important role in surface effects, even though the densities are low.

These atmospheric constituents collide with the spacecraft and its local gaseous atmosphere at orbital velocity, leading to two major types of interaction: gas-phase reactions and gas–surface reactions. Figure 1 provides an illustration of these interactions. The gas-phase reactions may be further broken down into a neutral component and a plasma component, and the gas–surface reactions may be broken into several components: surface-catalyzed reactions, surface neutralization of ions, chemical reactions with surfaces, and inelastic collisions. Because of their strong connection with surface charging phenomena,[2] we will not discuss ion–surface collisions; reference is made to two recent comprehensive reviews.[3,4] Likewise, inelastic collisions between the atmosphere and surfaces represent a very specialized topic intimately connected with atmospheric density measurements. Readers are referred to well-established reviews.[5–9] The aim of this review is to present a concise summary of work on spacecraft–atmosphere interactions, to present, when possible, ideas about the implications of the results, and to suggest work that needs to be done still. Gas-phase reactions will be considered first, followed by gas–surface interactions.

Gas-Phase Interactions

A dramatic indication of the transition from the dense local atmosphere of a spacecraft to the ambient atmosphere is shown in Fig. 2, which presents pressure-gauge data obtained on STS-39. The pressure gauge was located on a free-flying satellite, which was in the bay at the beginning of the flight. The free-flyer was then lifted by the shuttle's arm and extended to about 20-m distance from the bay with the pressure gauge facing in the ram; later the arm was rotated so that the pressure gauge was facing the wake of the shuttle. The pressure-gauge reading while the free-flyer is in the bay is approximately 1.5×10^{-6} torr (almost 100 times the ambient pressure). When the arm is extended, the pressure reading drops by a factor of almost 10, and with the pressure gauge facing the wake, the pressure reading is below the sensitivity of the gauge.[10]

In the following discussion, reactions of the ambient atmosphere with the spacecraft atmosphere will be divided into two sections: reactions with engine exhaust and reactions with outgassed molecules. The reason for this division is that the engine plumes have some directional properties (velocity ≈ 3.5 km/s), whereas outgassed molecules (principally water) are isotropically distributed and generally have thermal velocities characteristic of the surface temperature (at 220 K, the most probable velocity for H_2O is 0.45 km s^{-1}). It is generally assumed that the orbital velocity is equivalent to the

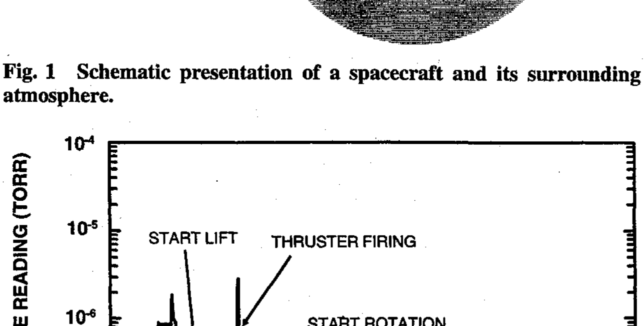

Fig. 1 Schematic presentation of a spacecraft and its surrounding atmosphere.

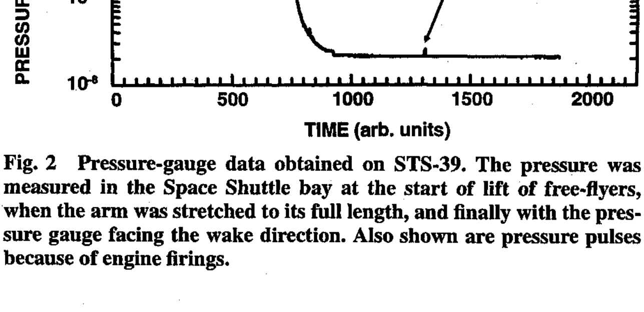

Fig. 2 Pressure-gauge data obtained on STS-39. The pressure was measured in the Space Shuttle bay at the start of lift of free-flyers, when the arm was stretched to its full length, and finally with the pressure gauge facing the wake direction. Also shown are pressure pulses because of engine firings.

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Table 1 Energetics of atmosphere–spacecraft gas collisions[a]

	Ram		Perpendicular		Wake	
	Speed, km/s	$E_{c.m.}$, eV	Speed, km/s	$E_{c.m.}$, eV	Speed, km/s	$E_{c.m.}$, eV
Plume–atmosphere	10.76	5.08	8.06	2.85	3.83	0.64
Outgas–atmosphere	7.71	2.61	7.27	2.32	6.88	2.08

[a]Assume that the spacecraft gas under discussion is H_2O and that the atmospheric gas is O
M_1 = (molecular weight of H_2O) = 18; m_2 = (molecular weight of O) = 16
μ = reduced mass = $(1/M_1 + 1/M_2)^{-1} = 8.47$
Collision energy = center-of-mass energy $E_{c.m.} = \frac{1}{2}\mu(\nu_1 - \nu_2)^2$
Orbital velocity at 300-km altitude = 7.726 km/s
Rotation velocity of the atmosphere = 470 m/s
Velocity of atmospheric species with respect to spacecraft = ν_2 = 7.256 km/s
Two scenarios: collision of atmospheric O with plume H_2O and with outgassed H_2O
ν_1 = (velocity of plume H_2O) = 3.5 km/s; velocity of outgassed H_2O (assuming surface temperature 220 K) = 0.45 km/s.

impact velocity of atmospheric species on the surfaces of the spacecraft. This assumption is, in fact, not exact, because the atmosphere rotates with respect to the Earth, and hence a correction for this effect has to be applied.[11] A spacecraft orbiting the Earth at 300-km. altitude in a circular orbit has a velocity of 7.726 km/s with respect to Earth (see Brown[12] for a discussion of this issue). The corotation of the atmosphere requires a correction of ≈0.47 km/s (the exact correction depends on the latitude, as discussed by King-Hele[11]), leading to a collision velocity of 7.256 km/s. For an O atom colliding with the surface, this leads to a collision energy of 4.37 eV. Table 1 presents a summary of the kinematics of these interactions after correction for the corotation of the atmosphere.

Reactions with Spacecraft Exhaust (Plume)

Most spacecraft in LEO maneuver and maintain altitude and attitude by the use of thrusters, which generally utilize hydrazine-based fuels. The combustion products collide with the atmosphere at high altitude and thus generate a complex chemical mixture. The energy available in the collision of the atmosphere with the plume products can be quite large and variable (depending on the angle of attack, as illustrated in Table 1). An enormous amount of information is available on plume phenomenology, since it is a subject that has many applications, such as contamination effects, surveillance, and tracking. For the case of the Space Shuttle, there are a number of measurements of the composition of the local atmosphere when thrusters are fired.[13–15] This paper will focus on those aspects of plume–atmosphere reactions that cause optical contamination in the vicinity of the spacecraft.

As the understanding of the effects of spacecraft contamination increased, it became important to develop a database and a predictive code. One of the earliest attempts at the development of a numerical prediction model came in the form of a fluid-dynamics model, CONTAM; in this model the combustion products formed in the chamber were calculated, allowing for incomplete combustion because of chamber design (nozzle shapes, etc.). The Shuttle nozzle, which had a wide angular spread, led to contaminant contours that themselves were widely spread. As a result, CONTAM was able to predict the deposition of contaminants on surfaces, even though the deposition occurred in a region where fluid flow was not applicable.[16] This early work showed that as a result of the incomplete combustion dangerous contaminants, including fuel droplets, are deposited on nearby surfaces. The predictions of the CONTAM code were verified by detailed experimental measurements in a vacuum chamber using a scaled-down motor.[16] Along with these measurements, the plasma diagnostic package (PDP) sensor suite (wavemeter, retarding potential analyzer, mass spectrometer, Langmuir probe) has provided valuable data on the exhaust from the Space Shuttle thrusters and on its modification of the local environment (contamination and disruption of the electromagnetic environment of the Space Shuttle).[17–20] For example, equilibrium calculations of thruster plume composition predict[16] that ≈95% of the exhaust consists of H_2O, N_2, H_2, CO, and CO_2. In contrast, the measurements show that there is a substantial amount of unburnt fuel and other condensable species, such as monomethyl hydrazine nitrate and hydrazine.[16]

More recently, a direct simulation Monte Carlo code, SOCRATES, has been developed for calculating the return flux and the optical background resulting from the interaction of the exhaust with the atmosphere.[21] It was found in this work that emission at 2.7 μm from the reaction $O_{atm} + H_2O_{exhaust} \rightarrow H_2O^* + O$ can extend up to 3 km from the point of origin for a VRCS engine firing in the ram direction at an altitude of 200 km. Similarly strong, but more confined spatially, emission in the ultraviolet was predicted at 306.4 nm [because of the transition $OH(A) \rightarrow OH(X)$] and subsequently confirmed by spaceborne observations.[22] Strong, extended optical emission (at $\lambda = 630$ nm) has also been observed using ground-based sensors.[23] This emission was found to depend on the angle of attack and to extend several kilometers from the point of origin. Its cause, collisional excitation of atmospheric $O(^3P)$ to the $O(^1D)$ state, was correctly modeled by SOCRATES.

There has been some speculation that the interaction of the engine exhaust with the atmosphere may be strongly affected by minor constituents, such as HCN and C_2H_2. Laboratory data suggest that such reactions are very efficient in generating excited molecular radiation in the near uv region of the spectrum.[24,25]

Interactions with Outgassed Species

Spacecraft surfaces are a source of thermal molecules in the spacecraft environment for two reasons: outgassing and desorption of deposited chemicals (such as from thrusters). The principal outgassed species is water, and it undergoes reactions with the atmosphere either on the surface or in the gas phase very close to the surface. The surface temperature varies between 200 K (night) and 350 K (day). Thus the surfaces provide a stable gaseous envelope for the spacecraft. The infrared telescope (IRT) flown on STS-5 observed[26,27] large signals at 2.7 μm, which were recently interpreted as being due to impact of hyperthermal atmospheric O atoms on outgassed water.[28] Similarly, the CIRRIS-1A instrument, flown on STS-39, measured[29] relatively high signals at 6.3 μm; these signals were attributed to collisional excitation of vibrational modes of H_2O by atmospheric O and N_2 molecules. A phenomenological cross section for this reaction has been derived from the space data,[28] the derived cross sections being 6.5×10^{-18}, 1×10^{17}, and 6.6×10^{-16} cm^2 for excitation of the ν_{001}, ν_{100}, and ν_{010} vibrational modes of H_2O. The analysis of the IRT data also led to the conclusion that charge exchange between O^+ and outgassed H_2O may play a significant role in the emission in the daytime emission in the 1.7–3.0-μm region.[28]

Plasma Effects

Even though the ion (mostly O^+) density (typically 10^5 cm^{-3}) is considerably lower than the neutral densities (typically 10^8 cm^{-3}), ion–molecule reactions play an important part in the composition of the local spacecraft atmosphere. Some aspects of plasma–spacecraft interactions—particularly as these interactions affect spacecraft charging and the operation of large spacecraft in LEO—have recently been reviewed by Hastings.[30] The importance of ionic effects is illustrated by the presence in the local atmosphere of the Space Shuttle of large quantities of H_2O^+ and H_3O^+ ions, which are not present in the normal atmosphere at 300 km.[31–33] Such ions clearly arise from charge-exchange reactions between ambient O^+ and outgassed H_2O, followed by reactions of the productions:

$$O^+ + H_2O \rightarrow H_2O^+ + O \tag{1}$$

$$H_2O^+ + H_2O \xrightarrow{k_2} H_3O^+ + OH \tag{2}$$

Since both H_2O and H_2O^+ have thermal velocities (the former is desorbed at near-thermal surface temperature, and the latter is formed mostly at rest), the appropriate value of k_2 is about[34] $3 \times 10^{-9} cm^3$ molecule^{-1} s^{-1}. Beyond this qualitative picture, it is somewhat difficult to achieve a quantitative analysis because of a number of factors that play a part in the ion–neutral phenomenology, as discussed elsewhere.[34] In the early analysis[35] densities for neutral H_2O were inferred from the ratio of O^+ to H_2O^+ in the shuttle environment. Later it was pointed out that the substantial energy dependence of the cross section for Eq. (2) meant that the measured density of H_3O^+ would depend on the relative velocities, i.e., the H_2O^+ velocity distribution.[34,36] The scenario is, in fact, even more complex because of the effects of the Earth's magnetic field and associated electric fields.[37,38] There has also been some speculation that an additional source of ionization (besides photoionization and charge exchange) has to be found to explain the large enhancements in plasma densities observed sometimes.[39,40] Surface charges complicate the situation further in two ways: 1) the movement of ions will not be represented by straight-line trajectories, meaning that the path length will be lengthened, and 2) the kinetic energy of the primary ion will be modified, so that the appropriate rate constants may be those at energies falling between thermal and hyperthermal kinetic energies.[34,36]

In addition to ion–neutral reactions between outgassed H_2O and ambient O^+, thruster firings generate other complex species, which affect the total ionized atmosphere of large space platforms. For example, in the study by Hunton and Machuzak[40] large amounts of N_2^+, not attributable to charge-exchange reaction with ambient O^+, were observed, leading the authors to conclude that an electron impact mechanism might be operative. As discussed in a previous section, minor constituents in the exhaust of engines may play a major role in the gaseous environment of large space structures in LEO. Recent laboratory measurements of the cross section of O^+ with a possible minor constituent, HCN, show that this can indeed be true. A hyperthermal total reaction cross section of $\approx 4 \times 10^{-15}$ cm^2 has been measured.[41] This cross section is equivalent to a rate coefficient of $\approx 3 \times 10^{-9}$ cm^3 molecule^{-1} s^{-1} for a ram burn.

If the ion density is very high, then ion neutralization may also be important. Two types of ion-neutralization reactions will be considered: electron–ion recombination in the gas phase, and ion neutralization on surfaces. Atomic ions (such as O^+) undergo two-body electron–ion recombination with a rate coefficient of $\approx 3 \times 10^{-12}$ cm^3 molecule s^{-1}. By contrast, molecular ions dissociatively recombine with electrons with a typical rate coefficient[42] of $\approx 10^{-7}$ cm^3 molecule s^{-1}. Thus, for the reaction

$$H_2O^+ + e \xrightarrow{k_3} \text{products} \tag{3}$$

where[43] $k_3 = 3 \times 10^{-7}$cm^3 molecule s^{-1} at $T = 300$ K, the time constant for reaction with electrons, τ_3, is given by $1/(k_3[e])$. For $[e] = 10^5$ cm^{-3}, τ_3 turns out to be ≈ 33 s. On the other hand, for the case of the Space Shuttle, the reaction (2) has $\tau_2 \sim 0.1$ s if $[H_2O] = 10^{10}$ cm^{-3}, as derived by Caledonia et al.,[35] suggesting that neutralization of H_2O^+ is unimportant. For spacecraft in LEO for long periods, it may be that outgassing is so reduced that $[H_2O]$ is diminished by a factor of 100 or more. Under that circumstance, ion–electron neutralization would become an efficient competitor with ion–neutral reactions. The net effect is that the depletion of electrons and ions in the extended vicinity of a spacecraft in LEO would lead to a modification of the plasma signature. A clear indication of neutralization was shown by experiments where Shuttle OMS engines were fired over the Millstone observatory.[44] An ionospheric bubble, depleted of electrons because of their recombination with molecular ions, was observed. In addition, emission from $O(^1D)$, a product of neutralization, was observed for several hundred kilometers. As will be discussed in the next section, H_2O^+ may play an important role in the daytime infrared (IR) signals in the vicinity of spacecraft.

The other type of ion neutralization that has been mentioned in connection with spacecraft in LEO is surface neutralization. Because of the large energies released in neutralizations (since ionization potentials are generally greater than 10 eV), there is opportunity for surface modification as well as for decomposition of molecular ions.[45] Low-energy scattering from clean and well-characterized single-crystal surfaces shows that a significant portion of the incident molecular ions are scattered from the surfaces without being neutralized or decomposed.[3,45] Ion–surface neutralization is affected by spacecraft charging, a subject that is beyond the scope of this survey (see, for example, a review on the subject of spacecraft charging by Garrett[46]).

Finally, electron impact ionization is worth mentioning briefly. Normally, in the LEO environment, electron impact ionization of the spacecraft atmosphere is unimportant. However, under special circumstances, the electrons of the atmosphere can be heated beyond the ionization potentials of some neutral molecules. For example, if the critical ionization velocity (CIV) phenomenon turns out to be valid, then electron impact ionization is implicitly involved in discharge formation. The CIV theory, postulated by Alfvén[47] to explain the formation of the solar system, proposes that neutral species traversing a weakly magnetized plasma at a velocity such that their kinetic energy is greater than their ionization potential are spontaneously ionized. Since it was first postulated, much theoretical work has been done to understand the basis of this theory. It is now thought that the injection of a fast neutral beam into a weakly magnetized plasma sets up disturbances that in turn generate waves that heat up the electrons on a very fast time scale.[48–52] The principal path for ionization is then electron impact. The evidence for CIV is controversial, and it remains to be shown whether the theory is applicable to conditions prevalent in the ionosphere.

Surface Effects

The aim of this discussion is not to present a tutorial on the subject of surface interactions; rather it is to present a concise summary of those aspects of surface chemistry which are important to the understanding of the interaction of the LEO environment with spacecraft. Two limits of interaction are as follows: 1) the gas species is reflected elastically from the surface, or 2) the gas species is accommodated completely (i.e., the surface acts as a system of coupled oscillators) and sticks to the surface. Reference is made to standard monographs on surface chemistry and surface physics for more basic discussion of the topic.[53–56]

Surface Erosion

Since a spacecraft in LEO travels at a velocity of ≈ 7.3 km/s with respect to the Earth's atmosphere, the collisions of the atmospheric constituents with spacecraft are very energetic: O and O^+ collide with surfaces at an energy of ≈ 4.4 eV, and N_2 does so at an energy of ≈ 7.6 eV. Such collisions are energetic enough that they may overcome reaction barriers, leading to surface modification or degradation.[57,58] An example of such interactions is the quick oxidation of silver films[59] and the removal of osmium films in LEO.[60] On the ground osmium is relatively inert at room temperature, oxidizing very slowly with the release of gaseous OsO_4. In LEO osmium is oxidized and removed very quickly.[60] Pioneering work by Leger and his co-workers[61] has shown that some of the earlier designs for the Space Station would suffer from structural weaknesses because of exposure to atomic oxygen during the expected 30-year life. A physical sputtering model for the removal of material in LEO has been suggested,[62] although confirming data are not presently available. The surfaces of some protective coatings, when exposed to LEO environment, change from being smooth to being corduroy-[63] or carpetlike,[64] thus making a detailed treatment of the observations somewhat difficult. Some surfaces have shown the formation of cones, suggesting that the velocity vector of the bombarding species plays an important role in the surface modification.[65] A treasure trove of space data related to surface interactions was obtained by the Long Duration Exposure Facility (LDEF), a mission whose lifetime in space was extended from six months to almost six years because of the Challenger disaster. The mission obtained long-term information on the effects of the space environment on thousands of materials. A summary of the observations is readily available,[66] although it should be kept in mind that analysis of the data is ongoing.

Further complicating the interpretation of space data is the difficulty in separating the effects of ionic and neutral species. In one experiment, Visintine et al.[64] placed a retarding grid over a sample plate and observed that the recision rate of the sample was the same as that of a similar plate where the retarding grid was held at 0-V potential. Thus the conclusion is drawn that removal of surfaces material is not due to charged particles. However, the experiment did not determine whether the surface modification is the same for ionic and neutral particles.

Surface-Catalyzed Recombination

This topic nowadays refers primarily, but not only, to the Shuttle glow phenomenon. Briefly, it was observed on the earliest Space Shuttle flights that the surfaces facing the ram direction had a visible glow extending perhaps about 15 cm from the surface.[67–70] This phenomenon is now known to be primarily due to emission from NO_2^* formed by the surface recombination of atmospheric O and adsorbed NO.[71–73] The current understanding of the phenomenon is that NO is deposited on spacecraft surfaces; O atoms from the ramming atmosphere then collide with the NO to form NO_2, which is electronically excited. This desorbed NO_2^* has a velocity that is normal to the surface, so that it escapes and radiates within a characteristic lifetime[74] of 0.3–1.3 ms. The Shuttle glow spectra that have been obtained so far show a continuum that is shaded to the blue[75] in comparison with the O + NO recombination spectrum obtained in laboratory studies.[76] Recently, an observation has been reported in the IR, suggesting that $NO_2(v)$ is present in the Shuttle glow.[77] All the explanations for the Shuttle glow phenomenon have centered on the surface-catalyzed neutral reactions. It is possible that ionic reactions, for example, $O^+ + NO_{adsorbed}$, may also play a role. In this case the product would be NO_2^+. Recent theoretical studies[78] suggest that the vibrational frequencies of NO_2^+ are similar to those of NO_2. The electronic spectrum of NO_2^+ is likely similar to that of CO_2, and would thus be expected to be present in the vacuum ultraviolet, near[79] 200 nm. Interestingly, a recent report suggests that there is indeed a component to the Shuttle glow in that region of the spectrum.[80]

Prior to the discovery of the Shuttle glow phenomenon, it was realized that surface-catalyzed reactions play a determining role in the mass-spectrometric measurements of atmospheric composition. Such measurements aboard satellites often show the products of recombination, rather than the nascent species. For example, the mass spectrometer aboard the DE-2 satellite indicated a large amount of O_2, where O atoms are expected.[81] The observation of O-atom recombination on spaceborne mass-spectrometer surfaces raises the question of whether there can be a component in the Shuttle glow spectrum because of O_2^* emission. For that to happen it would be necessary that O atoms be adsorbed on the surface so that they might be picked up by an incoming, fast, atmospheric O atom. Two potential mechanisms for that exist:

1) Exhaust from engines contains some O atoms that have velocities considerably less than the orbital velocity; thus they can be scattered and stick on the surfaces.

2) Another possibility is that an atmospheric O atom collides with the shuttle surfaces and accommodates immediately (i.e., it adsorbs on the surface), thereby becoming a target for an incoming O atom. Normally accommodation would require several collisions. However, shuttle tile surfaces may be thought of as composed of coupled vibrators or springs, which are able to absorb a large amount of energy upon impact by incoming atmospheric species (this because the tiles are basically composed of silica tubes fused together to provide thermal protection with least mass).

Conclusions

The objective of this review has been to present a summary of work in an area of research that is likely to become more important as spaceborne platforms acquire increased importance in the fulfillment of national needs. Clearly the most important outcome for these studies is the development of numerical models that can provide reliable predictions of the outcome of particular operations in space. In that connection, deficiencies in understanding the role of ionization and ionic process in space, lack of information about the accommodation of gases and radicals on noncrystalline surfaces (such the shuttle tiles) and about ion neutralization on semiconductor amorphous surfaces, and the difficulty in making controlled studies of the effect of surface charging on ion densities and composition will hamper the development of a numerical model that integrates molecular processes, plasma phenomena, and charging phenomena.

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