

Aeronomy of CO₂ Atmospheres: A Review

T. M. DONAHUE

Dept. of Physics, The University of Pittsburgh, Pa.

(Manuscript received 8 April 1971, in revised form 9 June 1971)

ABSTRACT

Data obtained by the UV spectrophotometer experiments and the radio occultation experiments on Mariners 6 and 7 indicate an atomic oxygen concentration of about 3% in the upper atmosphere, an exospheric temperature of about 350K, and a very low solar EUV heating efficiency for Mars. Laboratory studies do not support mechanisms for rapid recombination of CO and O in the upper atmosphere. Transport appears to control the O concentration. However, there is still a problem of accounting for CO-O₂ recombination in the lower atmosphere. A satisfactory self-consistent explanation of all of the Mariner and Venera upper atmosphere data for Mars and Venus still has not been produced. Difficulties with the presently recommended low EUV solar fluxes and high Martian airglow brightness are discussed.

1. Introduction

As we reached the end of this conference devoted to the carbon dioxide atmospheres of Mars and Venus, several questions, unresolved for some time, seemed to have been answered. Those pertained to the efficiency of heating by the solar ultraviolet flux, the temperature of the upper atmosphere, and the relative roles of transport and local chemical recombination in determining the degree of dissociation in the upper atmosphere. Other very basic problems still remain with us, however. Outstanding among these is how to control the abundance of CO and O₂ in the lower atmosphere in view of the lack of any effective, known gas-phase recombination mechanism. Furthermore, careful consideration indicates that even the apparently settled state of the other problems may be an illusion.

To appreciate these assertions it is useful perhaps to return and review the state of affairs after the second Tucson Conference, devoted mainly to Venus, three years ago. At that time the flight of Mariner 4 (Kliore *et al.*, 1965) and spectroscopic observations from earth (Belton and Hunten, 1966) had revealed that the lower atmosphere of Mars was composed almost entirely of CO₂, and had also given us the profiles of temperature and densities up to about 30 km. From a theory of UV heating and cooling by conduction and IR radiation, McElroy (1967, 1969b) had produced a model for the thermal structure and composition of this atmosphere as high as the exosphere. This model was based on a calculation of heating efficiency developed by Henry and McElroy (1968) which called for 30% of the solar energy deposited to be converted locally into heat. This was after global averaging had taken account of a transport of half the solar energy input to the

nightside of the planet. The radio occultation experiment on Mariner 4 had given us the electron density profile in the ionosphere, a surprising single layer with a maximum at about 125 km. The atmospheric model of McElroy did not quite satisfy the conditions I had shown to be necessary if this layer was to be of the F1 type (Donahue, 1966). An early attempt by Chamberlain and McElroy (1966) to describe it as an E layer had foundered when it was shown that the recombination coefficient of CO₂⁺ was not particularly large (Weller and Biondi, 1967). To correct the large scale height of the ionospheric topside resulting from the high exospheric temperature, Cloutier *et al.* (1969) proposed that the solar wind flowing into the ionosphere and becoming loaded with the ionospheric ions depressed the scale height to that of the neutral atmosphere.

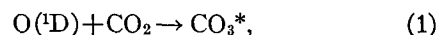
In any event it was clear that the absence of anything like an F2 layer and the small scale height of the topside severely limited the admissible concentration of atomic oxygen in the upper atmosphere (Donahue, 1966). Estimates of the amount which could be tolerated ranged between about 1 and 10% at the 120-km level. Obviously, to maintain such a low degree of dissociation in the thermosphere was not a trivial matter. But for the planet as a whole, spectroscopic limits had been placed on the mixing ratios of O₂ and CO, *viz.*, 2.3×10^{-3} and 8×10^{-4} , respectively (Belton and Hunten, 1968; Connes *et al.*, 1968). Thus, a two-fold difficulty confronted us: how to obtain low densities of O in the thermosphere and how to keep O₂ and CO from building up in the lower atmosphere in view of the slow rate of recombination of CO and O compared to the three-body association of atomic oxygen.

At the time of the Second Conference, Venus had just been explored by Mariner 5 and Venera 4 (Mariner Stanford Group, 1967; Avduvsky *et al.*, 1969). In the case of that planet the electron density profile measured by radio occultation agreed very well with the McElroy model (1968) which called for a straightforward F1 layer. The exospheric temperature in the model, 650K, was precisely that implied by the Lyman α data obtained with the UV photometer on Mariner 5 (Barth *et al.*, 1967) when the results were interpreted in terms of resonance scattering by exospheric hydrogen. The explanation of ionospheric data (again as in the case of Mars) appeared to preclude large concentrations of atomic oxygen. The limit was set by the requirement that there not be too much O^+ to accord with the rapid decrease in electron density with altitude above the F1 peak. This requirement was consistent with the failure of Kurt *et al.* (1969) to find atomic oxygen airglow from Venera 4 on the nightside of the planet. However, Moos *et al.* (1969) reported observing a bright feature near 1300Å from Venus with a rocketborne spectrophotometer. If their measurement had been taken at its face value it would have meant an emission rate of about 3 kR in the OI resonance triplet, and could have, though not necessarily, implied a lot of oxygen. Various excuses were found not to take these rocket results seriously.

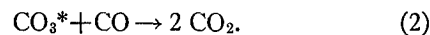
The McElroy thermospheric structure model worked well for Venus but had to be doctored by a solar wind interaction with the ionosphere on Mars. Sometime later Stewart and Hogan (1969a) pointed out that if the heating efficiency of the solar ultraviolet on Mars was 0.16 (after averaging for the planet's rotation) the exospheric temperature would be reduced and the ionospheric F1 model brought into agreement with observation without the help of the solar wind. They proposed that the efficiency be effectively doubled on Venus because of the presumed slow rotation of the upper atmosphere. Thus, they would use a value of 0.30 on Venus and this would be the same as the effective value used by McElroy after he had allowed for global averaging.

In any event there has been general agreement that the characteristics of the ionosphere require that the abundance of atomic oxygen be low in the atmospheres of both planets. The problem is how to keep it low. On Mars, for example, enough oxygen atoms are created in about 5×10^4 sec by photolysis of CO_2 to make the concentration three parts per hundred in the lower thermosphere. Thus, if the steady-state ratio of O to CO_2 is 3% (as the Boulder group infers from airglow data), it is necessary to dispose of three parts in 100 of O atoms in 5×10^4 sec. Recombination *in situ* at the 10^{11} cm^{-3} CO_2 level would have to proceed via a reaction with a rate constant of about 1.5×10^{-24} cm^6 sec^{-1} to achieve this goal. Two-body radiative association of CO and O would need a rate constant of

2×10^{-13} cm^3 sec^{-1} . Both are unrealistic. These requirements led McElroy to adopt the CO_3 mechanism (suggested by some laboratory work):



followed by



As I pointed out at the Second Conference (Donahue, 1969), this mechanism required that the unstable CO_3^* complex live for 10–100 sec before breaking up. McElroy and Hunten (1970) later modified the first step to stabilize the CO_3 by photon emission. Even so, the lifetime of CO_3 , or the collision time during which a photon must be radiated, had to be in the neighborhood of 10^{-7} sec, or 10^5 vibrational periods.

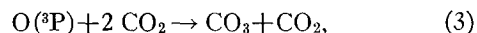
There were, therefore, three solutions to the atomic oxygen problem: 1) chemical recombination occurred *in situ* via a fast route such as that proposed by McElroy; 2) CO_2 was not dissociated by solar ultraviolet under the low pressure conditions prevailing in a planetary upper atmosphere; or 3) fast downward transport (or perhaps lateral transport) carried the products of photolysis out of the production region. The effective eddy diffusion coefficient needed for this transport is in the neighborhood of 10^7 cm^2 sec^{-1} on Mars (Hanson¹; McElroy and Hunten, 1970b).

2. Present situation

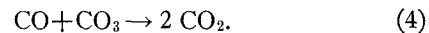
At this Conference we have heard a review (Clark, 1971) of the excellent work of Clark and Noxon (1970), Young (1970), and Slinger and Black (1970). We know that:

- 1) CO_2 does dissociate in photolysis by ultraviolet even at the low pressures of an upper atmosphere even though all problems concerning the quantum efficiency may not have been resolved below 1740Å.
- 2) Collisions between CO_2 molecules and metastable oxygen atoms in the 1D state very effectively quench the excited state with unit probability for producing a ground state atom after the collision.

No support can be found in these laboratory studies for the CO_3 recombination mechanism involving $O(^1D)$. Clark has brought up a new mechanism involving ground state atoms, i.e.,



followed by



This scheme depends on a lack of competition from O and CO_3 reactions. Let us hope that the vestiges of these recombination schemes will not hang around for

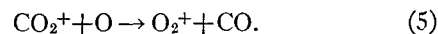
¹ Hanson, W. B., 1971: A statement of the aeronomical problems of CO_2 atmospheres. Paper presented at the Fifth Arizona Conference, Tucson.

long in a state supported only by speculation. It is true that it would be a blessing, for the sake of avoiding an O₂-CO problem, if we could get the CO₂ back together in the thermosphere. However, I am really skeptical that a process as efficient as the one we are hunting for would have eluded the intense search which has been made for it during the past several years. Besides, if A. I. Stewart's (1971) treatment is correct, it is useful to avoid releasing the chemical energy to heat the thermosphere by transporting the O and CO down below the mesopause.

So the message at this Conference seemed to be that we had better look for transport to get rid of the dissociation products. If the analysis of Thomas (1971) is correct, the abundance ratios of 10⁻³ for O to CO₂ that were with us for a while and required effective mixing coefficients that were in the realms of fantasy have been corrected to about 3 × 10⁻² on Mars. An eddy diffusion coefficient as small perhaps as 10⁷ cm² sec⁻¹ would seem to be able to cope with the transport requirements in this case. Dickinson (1971) has given us a novel picture of the Venus circulation. As a result of heat deposition well above the level of radiative cooling on that planet, he claims that very rapid horizontal transport would occur from the day- to the nightside of the planet. This motion would also be accompanied by some fairly rapid vertical movement. The result would be a very great diurnal temperature variation and the possibility of sweeping the photolysis products around to the darkside where they could recombine. Unfortunately, this picture doesn't develop for Mars where we have more information about our needs. On Mars the F1 and reference levels are at about the same altitude. I have sensed, however, that our experts on dynamics did not find our demands on Martian transport to be extreme. So we left the Conference moderately hopeful that downward mixing is the answer to the atomic oxygen problem on Mars.

Our fund of hard information concerning the Martian upper atmosphere has been greatly increased as a result of the data obtained on Mariners 6 and 7. The excellent results of Barth's group on UV airglow observations have revolutionized our picture of the upper atmosphere. The great surprise was the brightness of the radiation, particularly in the CO Cameron band system and in the atomic oxygen forbidden lines. If Hinteregger's suggested revision of the solar UV fluxes is correct, about half the incident solar EUV radiation comes back out of the atmosphere as airglow according to A. I. Stewart (1971). The analysis of the CO₂⁺ band data, the Cameron bands, and the OI ¹S-³P line by Stewart indicates that all of these emissions are produced as a result of photon and electron processes involving CO₂. He has shown that the results are reproduced best in an atmospheric model which he

produces by utilizing only 0.19/2 of the solar flux² in heating. The rest is lost in UV and IR airglow and in transport of about 30% of the energy by O and CO into the lower atmosphere. The result is an atmosphere which would be described by an exospheric temperature of only about 350K [compared to 480K predicted by Stewart and Hogan (1970a,b)]. Although other models are possible according to A.I. Stewart none have high exospheric temperatures. Unfortunately, the model I have just described—the one which fits the data best—involves an ionosphere containing 30% CO₂⁺ ions. Atomic oxygen concentrations as large as those now being quoted would produce an ionosphere of about 90% O₂⁺ at the F1 peak as a result of the reaction



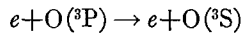
According to this analysis the two massive factors which reduce the heating efficiency from 66% as used by McElroy to 19% are the CO and O airglow re-radiation and the transport of chemical energy out of the thermosphere. The neglect of both is certainly forgivable. Such efficient excitation of the Cameron bands was certainly unexpected and is still not supported by laboratory measurements. As for the second source of heating it was in the spirit of McElroy's work to pursue models in which recombination occurred locally. Of course, A. I. Stewart's work supports the supposition that this is not the case and that transport is required to hold down the atomic oxygen concentration.

Using A. I. Stewart's model for the atmosphere, the thermal structure, and the photoelectron fluxes, Thomas and Strickland (Thomas, 1971) have analyzed the atomic oxygen airglow lines and obtained a best fit with a model containing about 3% atomic oxygen at 120 km. The main source of excitation of the oxygen lines is photoelectron impact on oxygen. The models presented at the Conference had the disquieting effect of predicting much more excitation at low altitudes than is actually observed. On the topside there was poor agreement between the observed and calculated profiles for the forbidden ⁵S-³P 1356Å lines. These were deficiencies which certainly had to be corrected before we could feel confident that all of the important information in the Mariner spectra has been extracted from the data. My first impression was that one could do a better job of fitting the data with less atomic oxygen and a higher exospheric temperature as suggested by McElroy and McConnell (1971).

Indeed, since the Conference, Thomas and Strickland (Thomas, 1971) have modified their radiative transport treatment to obtain much better agreement with the data, still without modifying the oxygen model. However, in a paper also appearing in this issue, McElroy and McConnell (1971), using what appears to be the

² The assumption here is the same made by McElroy, i.e., that the heating is that produced by a sun shining for half a day at a zenith angle of 60°.

same radiative transport technique used by the Boulder group, obtain an equally good fit to the Mariner 1304Å data with a much thinner oxygen model and a much lower exospheric temperature. The best fit is with $5 \times 10^7 \text{ cm}^{-3}$ oxygen atoms at 125 km and an exospheric temperature of 435K. The reason for the discrepancy is not hard to find. McElroy and McConnell assert that they have used the full energy dependence of the cross section for



measured by Stone and Zipf (1971) in computing the rate at which oxygen is excited by photoelectrons. Thomas and Strickland, on the other hand, have used a rate calculated for a different cross section by A. I. Stewart but simply scaled in bulk to accommodate the Stone and Zipf results. McElroy and McConnell³ obtain a source represented by $1.8 \times 10^{-7} e^{-1.5 \times 10^{-17} (N/\mu)}$, while Thomas uses $1 \times 10^{-7} (N/\mu)^{-2} [\text{sec}^{-1}]$, where N is the columnar content of the atmosphere. This is a discrepancy which must be resolved since the atomic oxygen abundances are significantly lower and the exospheric temperatures significantly higher in the Harvard model than in the Boulder model.

Concerning Venus, we have heard Moos⁴ confirm the very interesting Johns Hopkins rocket spectra (Moos *et al.*, 1969). At least two sets of remarks can be made concerning these beautiful spectra. First, as A.I. Stewart (1971) and Thomas (1971) have remarked, the 6 kR of OI 1304Å airglow compared to 0.5 kR in the zenith on Mars scales nicely if the factor of 4 in solar flux (affecting photoelectron flux in particular) is combined with a threefold greater atomic oxygen abundance on Venus than on Mars. The 3 kR of 1356Å airglow compared to 1/50 times as much in the zenith on Mars will be more difficult to cope with.

The second comment pertains to the observation of only 24 kR of Lyman α . This is about what would be expected from the so-called hydrogen Lyman α component in the Mariner 5 photometer data alone. Inclusion of the so-called mass 2 component would lead to an expectation of about 90 kR. Since the present rocket results are essentially the same as those obtained from the previous rocket during the same epoch as the Venus fly-by, the suggestion here is that 24 kR is the proper Lyman α emission rate and that the troublesome mass 2 component was somehow spurious. This would be a welcome (if dull) solution to the deuterium- H_2 problem on Venus. Those of us who explored the deuterium hypothesis have consistently pointed out that it implies great enrichment of Venus in deuterium unless mixing of dissociation products into a recombination zone is very weak. The requirement of very inefficient transport tends to conflict with the opposite need for

O-CO recombination. On the other hand, it is very difficult to see how any parasitic effect in the Mariner experiment would have produced just a factor of 2 in scale height compared to the proper result.

Some interesting features of the radio occultation data discussed by Rasool and Stewart (1971) are the temperatures below the CO_2 condensation point now being inferred 30 km or so above the surface of Mars, the satisfying verification of the surface discontinuity predicted by Gierasch and Goody (1968), and the large values obtained for the maximum electron density (Rasool and Stewart, 1971). The observed peak densities of $2 \times 10^5 \text{ cm}^{-3}$ must be compared with predicted values in A.I. Stewart's (1971) models that range from $7 \times 10^4 \text{ cm}^{-3}$ (CO_2^+ predominant) to $1 \times 10^5 \text{ cm}^{-3}$ (O_2^+ predominant).

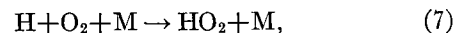
3. Discussion and conclusions

As of the end of the Conference we found ourselves presented with a fairly coherent picture for the aeronomy of the upper atmosphere of Mars during solar minimum. According to this picture the photolysis products of CO_2 were transported down from the thermosphere rapidly enough to keep the oxygen relative number density at about 3% in the F1 region. The heating efficiency in the sunlit hemisphere was only about 0.10 as a result of planetary averaging, intense radiative cooling in the ultraviolet, and transport of O and CO out of the thermosphere. The thermospheric temperature accordingly was only about 350K.

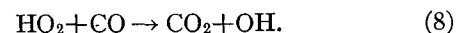
Having said this much, I must quickly add that major problems remained. Foremost of these was still the question of how CO and O ultimately recombine. The ratio of O_2 to CO_2 is less than 2.3×10^{-3} and the ratio of CO to CO_2 is 8×10^{-4} on Mars. A similar CO_2 abundance, and much less O_2 , are present on Venus. Yet three-body association of atomic oxygen to form O_2 is much more efficient than



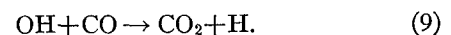
Some very effective method must be found to combine the O_2 molecules which originate from CO_2 photolysis with carbon monoxide. One scheme proposed in the past (Donahue, 1969; McElroy and Hunten, 1970) is to form HO_2 from oxygen molecules



with hydrogen atoms being obtained, let us say, from dissociation of water; and then react the HO_2 with CO, according to



The hydroxyl can then be used to recombine the other oxygen atom and restore the hydrogen catalyst through the very fast reaction



³ See legend to their Fig. 1 on p. 880.

⁴ Moos, H. W., 1971: Ultraviolet spectrum of Venus between 1200–1900 Å. Paper presented at the Fifth Arizona Conference, Tucson.

Unfortunately, Kaufmann's⁵ demotion of (8) to a rate constant of only 10^{-23} or 10^{-24} $\text{cm}^2 \text{sec}^{-1}$ (Baldwin *et al.*, 1970) knocks this chain out. With it goes the only gas-phase mechanism so far suggested. We are left, on Mars as on Venus, with the possible need for recombination on solid surfaces. If the site of the recombination is to be close to the planetary surface, we are then forced to increase the demands on the mechanism which transports the dissociation products downward. The distance they must be carried in half a day becomes of the order of 50–100 km rather than a scale height or two. Effective mixing coefficients in excess of 10^8 $\text{cm}^2 \text{sec}^{-1}$ are then required, and our past explanations begin to collapse.

And, indeed, the paper by McElroy and McConnell (1971) bears out this gloomy prophesy. To accommodate the low atomic oxygen densities in their model and to maintain the small abundances of O_2 and CO in the lower atmosphere by transport right into the Martian soil, they show that an effective eddy diffusivity of 5×10^8 $\text{cm}^2 \text{sec}^{-1}$ would be needed. The vertical flow velocities entailed are several hundred centimeters per second.

One wonders also how well A. I. Stewart's explanation of the aeronomy of Mars for the time of Mariner 6 and 7 will fare when it is confronted with the problem of explaining the famous electron density profile of Mariner 4. Using at least three times as much solar UV flux and almost twice as great a heating efficiency as A. I. Stewart (1971) uses for 1969, Stewart and Hogan were able to account for the ionosphere in 1965. And how will an efficiency of 0.19/2 ever explain the 650K exospheric temperature and the ionosphere on Venus in 1967 when McElroy's value of 0.66/2 worked so well?

We all wonder, in fact, in what way the solar EUV fluxes we are using are related to reality. Current calculations follow Hinteregger's recipe and use his 1965 values reduced by a factor of 3. The ionization rates fail by a factor of almost 3 to produce the observed electron densities. Increasing the fluxes so greatly would result in much greater thermospheric temperatures [100K increase for a 60% increase in flux according to A. I. Stewart (1971)] and the ionospheric profiles along with the airglow features would then disagree with observation.

In this issue, as a post-conference paper, R. W. Stewart (1971) makes the interesting suggestion that ionization by the solar wind protons which penetrate the bow shock may provide the missing ionization source. Remaining to be discovered is whether quantitative theory will permit this mechanism to survive.

Related, perhaps, to the problem of ionization and solar fluxes is the difficulty with A. I. Stewart's assumption that the $a^3\Pi$ state of CO is excited every time it is

energetically possible. This is far from borne out in laboratory experience. Obviously, the bright Cameron band emission would not be such a large fraction of the solar flux if the latter quantity were increased by a factor of 3. The challenge is to produce an atmosphere which will account for all the Mariner 6 and 7 data with the help of such great solar radiation.

It should be clear from these remarks that I don't feel that the major aeronomic problems of CO_2 atmospheres are resolved yet. And it should also be clear that I consider the extensive work performed prior to Mariners 6 and 7 by intrepid spirits such as McElroy to have been invaluable in setting forth the important elements of the subject. Where they have failed—if they have failed—to produce models in accord with reality, it seems to have been because of such unexpected effects as the intense airglow in the CO Cameron bands.

Acknowledgments. This work was supported by the National Science Foundation, Atmospheric Sciences Section (Aeronomy), under Grant GA-18224.

REFERENCES

- Avduevsky, V. S., M. Ya. Marov and M. K. Rozhdestvensky, 1969: Model of the atmosphere of the planet Venus based on results of measurements made by the Soviet automatic interplanetary station Venera 4. *The Venus Atmosphere*, New York, Gordon and Breach, 79–104.
- Baldwin, R. R., R. W. Walker and S. J. Webster, 1970: Carbon monoxide sensitized decomposition of hydrogen peroxide. *Combustion Flame*, **15**, 167–172.
- Barth, C. A., J. B. Pearce, K. K. Kelly, L. Wallace and W. G. Fastie, 1967: Ultraviolet emissions observed near Venus from Mariner 5. *Science*, **158**, 1675–1678.
- Belton, M. J. S., and Donald M. Hunten, 1966: The abundance and temperature of CO_2 in the Martian atmosphere. *Astrophys. J.*, **145**, 454–467.
- , and —, 1968: A search for O_2 on Mars and Venus: A possible detection of oxygen in the atmosphere of Mars. *Astrophys. J.*, **53**, 963–967.
- Chamberlain, J. W., and M. B. McElroy, 1966: Martian atmosphere: The Mariner occultation experiments. *Science*, **152**, 21–22.
- Clark, I. D., and J. F. Noxon, 1970: Photodissociation of CO_2 on Mars. *J. Geophys. Res.*, **75**, 7307–7310.
- Cloutier, P. A., M. B. McElroy and F. C. Michel, 1969: Modification of the Martian ionosphere by the solar wind. *J. Geophys. Res.*, **74**, 6215–6228.
- Connes, P., J. Connes, L. D. Kaplan and W. S. Benedict, 1968: Carbon monoxide in the Venus atmosphere. *Astrophys. J.*, **152**, 731–743.
- Dickinson, R. W., 1971: Circulation and thermal structure of the Venusian thermosphere. *J. Atmos. Sci.*, **28**, 885–894.
- Donahue, T. M., 1966: Upper atmosphere and ionosphere of Mars. *Science*, **152**, 763–764.
- , 1969: The upper atmosphere of Venus: A review. *The Venus Atmosphere*, New York, Gordon and Breach, 511–529.
- Felder, W., W. Morrow and R. A. Young, 1970: Experimental evidence of the photochemical instability of a pure CO_2 planetary medium. *J. Geophys. Res.*, **75**, 7311–7314.
- Gierasch, P., and R. Goody, 1968: A study of the thermal and dynamical structure of the Martian lower atmosphere. *Planetary Space Sci.*, **16**, 615–646.

⁵ Kaufman, F., 1971: Reactions of some minor constituents in CO_2 atmospheres. Paper presented at the Fifth Arizona Conference, Tucson.

- Henry, R. J. W., and M. B. McElroy, 1968: Photoelectrons in planetary atmospheres. *The Atmospheres of Venus and Mars*, New York, Gordon and Breach, 251-279.
- Hogan, J. S., and R. W. Stewart, 1969: Exospheric temperatures on Mars and Venus. *J. Atmos. Sci.*, **26**, 332-337.
- Hunten, D. M., and M. B. McElroy, 1970: Production and escape of hydrogen on Mars. *J. Geophys. Res.*, **75**, 5989-5995.
- Kliore, A., D. L. Cain, G. S. Levy, V. R. Eshleman, G. Fjeldbo and F. D. Drake, 1965: Occultation experiment: Result of the first direct measurement of Mars' atmosphere and ionosphere. *Science*, **149**, 1243-1245.
- Kurt, V. G., S. B. Dostovalov and E. K. Sheffer, 1969: The Venus far ultraviolet observations with Venera 4. *The Venus Atmosphere*, New York, Gordon and Breach, 477-485.
- Mariner Stanford Group, 1967: Venus ionosphere and atmosphere as measured by dual frequency radio occultation of Mariner 5. *Science*, **158**, 1678-1681.
- McElroy, M. B., 1967: The upper atmosphere of Mars. *Astrophys. J.*, **150**, 1125-1138.
- , 1968: The upper atmosphere of Venus. *J. Geophys. Res.*, **73**, 1513-1521.
- , 1969a: The upper atmosphere of Venus in light of the Mariner 5 measurements. *The Venus Atmosphere*, New York, Gordon and Breach, 487-495.
- , 1969b: Structure of the Venus and Mars atmospheres. *J. Geophys. Res.*, **74**, 29-41.
- , and Donald M. Hunten, 1970: Photochemistry of CO₂ in the atmosphere of Mars. *J. Geophys. Res.*, **75**, 1188-1201.
- , and J. C. McConnell, 1971: Dissociation of CO₂ in the Martian atmosphere. *J. Atmos. Sci.*, **28**, 879-884.
- Moos, H. W., W. G. Fastie and M. Bottema, 1969: Rocket measurement of ultraviolet spectra of Venus and Jupiter between 1200A and 1800A. *Astrophys. J.*, **155**, 887-897.
- Rasool, S. I., and R. W. Stewart, 1971: Results and interpretation of the S-band occultation experiments on Mars and Venus. *J. Atmos. Sci.*, **28**, 869-878.
- Slanger, T. G., and G. Black, 1970: The CO₂ photolysis problem. *Trans. Amer. Geophys. Union*, **51**, 786.
- Stewart, A. I., 1971: Mariner 6 and 7 ultraviolet spectrometer experiment: An interpretation of the intense CO₂⁺, CO and O airglow emissions. *J. Geophys. Res.* (in press).
- Stewart, R. W., 1971: The electron distributions in the Mars and Venus upper atmospheres. *J. Atmos. Sci.*, **28**, 1069-1073.
- , and J. S. Hogan, 1969a: Empirical determination of heating efficiencies in the Mars and Venus atmospheres. *J. Atmos. Sci.*, **26**, 330-335.
- , and —, 1969b: Solar cycle variation of exosphere temperatures on Mars and Venus: A prediction for Mariner 6 and 7. *Science*, **165**, 386-387.
- Stone, E. J., and E. C. Zipf, 1971: Excitation of the OI(³S) and NI(⁴P) resonance states by electron impact on O and N. *Phys. Rev. Letters* (in press).
- Thomas, G. E., 1971: Neutral composition of the upper atmosphere of Mars as determined from the Mariner UV spectrometer experiments. *J. Atmos. Sci.*, **28**, 859-868.
- Weller, C. A., and M. A. Biondi, 1967, Measurements of dissociative recombination of CO₂⁺ ions with electrons. *Phys. Rev. Letters*, **19**, 52.