Diurnal Variation of Stratospheric Chlorine Monoxide: A Critical Test of Chlorine Chemistry in the Ozone Layer

P. M. Solomon, R. de Zafra, A. Parrish, J. W. Barrett

Abstract. *This article reports measurements of the column density of stratospheric chlorine monoxide and presents a complete diurnal record of its variation (with 2-hour resolution) obtained from ground-based observations of a millimeter-wave spectral line at 278 gigahertz. Observations were carried out during October and December 1982 from Mauna Kea, Hawaii. The results reported here indicate that the mixing ratio and column density of chlorine monoxide above 30 kilometers during the daytime are ~ 20 percent lower than model predictions based on 2.1 parts per billion of total stratospheric chlorine. The observed day-to-night variation of chlorine monoxide is, however, in good agreement with recent model predictions, confirms the existence of a nighttime reservoir for chlorine, and verifies the predicted general rate of its storage and retrieval. From this evidence, it appears that the chlorine chemistry above 30 kilometers is close to being understood in current stratospheric models. Models based on this chemistry and measured reaction rates predict a reduction in the total stratospheric ozone content in the range of 3 to 5 percent in the final steady state for an otherwise unperturbed atmosphere, although the percentage decrease in the upper stratosphere is much higher.*

Chlorine monoxide (ClO) has for some years been recognized as a key tracer of the stratospheric ozone depletion cycle arising from natural and anthropogenic injection of chlorine-containing compounds, principally halocarbons, into the atmosphere (*1*, *2*). The reactions

$$O_3 + Cl \rightarrow ClO + O_2 \quad (1)$$

and

$$ClO + O \rightarrow Cl + O_2 \quad (2)$$

constitute the catalytic cycle by which chlorine atoms convert ozone, O_3, to diatomic O_2.

There is a strong diurnal variation expected in the concentration of ClO. After the recombination of atomic oxygen at sunset, reaction 2 ceases. At night, ClO is believed to combine in a three-body reaction with NO_2 to form chlorine nitrate,

$$ClO + NO_2 \xrightarrow{M} ClONO_2 \quad (3)$$

which is thought to be the dominant reservoir of chlorine in the absence of sunlight. During daylight hours, free chlorine is again produced from this reservoir by the photolysis of chlorine nitrate:

$$ClONO_2 + h\nu \rightarrow Cl + NO_3 \quad (4)$$

The rate of nighttime removal of ClO via reaction 3 is dependent on the NO_2 concentration and the total density, both of which decrease with altitude above 30 km: thus high-altitude ClO is expected to last through the night, while ClO at lower levels (altitude $\lesssim$ 35 km) disappears. Earlier measurements by in situ resonance fluorescence (*3*), infrared heterodyne spectroscopy (*4*), balloon-borne (*5*) and ground-based (*6*) millimeter-wave spectroscopy have established the presence, approximate quantity, and vertical distribution of daytime stratospheric ClO. A more critical test of the full complex of reactions of stratospheric chlorine may be obtained from measurements of the diurnal variation of ClO. Such observations avoid the complications and uncertainties introduced by vertical and lateral transport and long-term seasonal trends. Earlier balloon-based millimeter measurements over a limited portion of the diurnal cycle have shown a decrease in ClO at sunset and an increase after sunrise (*5*). In this article we present a complete diurnal record of ClO variation, with a time resolution of 2 hours, acquired by ground-based remote sensing of millimeter-wave line emission.

P. M. Solomon is professor of astronomy and R. de Zafra is professor of physics at the State University of New York, Stony Brook 11794. H. Parrish and J. W. Barrett are research associates at the same institution.

Observations of Emission Lines

The ClO molecule has millimeter-wave rotational spectral lines spaced approximately every 37 GHz. We have reported measurement (*6*) of the line at 204.352 GHz from the $J = 11/2 \rightarrow 9/2$ levels. Our current measurements are based on the $J = 15/2 \rightarrow 13/2$ transition at 278.630 GHz. We use a cryogenically cooled millimeter-wave heterodyne mixer receiver with a noise temperature of 1100 K, approximately 2½ times more sensitive than our earlier detector (*6*). Use of this more sensitive detector, combined with an increase by a factor of 2.4 in the theoretical line intensity for the higher frequency 278-GHz line as compared with the 204-GHz line, has led to a sixfold increase in observational sensitivity. For a fixed signal-to-noise ratio, the required measurement duration is reduced by about a factor of 6^2 or 36, allowing a relatively high time resolution to be achieved. The "back-end" spectrometer consists of a filter bank with 256 channels, each with a bandwidth of 1 MHz. The measurement technique, calibration method, and instrumental configuration described earlier (*6*) remain unchanged.

Our observations were carried out at the summit of Mauna Kea, Hawaii (elevation, 4250 m; latitude, 19.5°N) during two periods, from 8 to 11 October and from 9 to 16 December 1982. The atmospheric water vapor content, which dominates the tropospheric absorption of stratospheric emission lines at millimeter-wave frequencies, was very low and generally stable around the clock during these observation periods (*7*).

In the following discussion, we present emission intensities as brightness temperatures in kelvins. This custom, commonly used in radio astronomy, is derived from the Rayleigh-Jeans approximation for blackbody radiation, in which emitted power per unit frequency is linearly proportional to temperature. All intensities represent the values that would be observed if one were looking through one stratospheric air mass toward the zenith after removing the effect of tropospheric attenuation.

In Fig. 1, we present a sample of midday (1230 to 1630) and nighttime

for the development of new products.

That picture represents a misunderstanding. Although MITI does indeed sponsor R & D programs, such as the highly publicized ones on integrated circuits and the fifth-generation computer, the R & D tends to be basic and engineering research. In the United States, such R & D efforts are centered in our universities.

The commercial R & D successes of Japan, as opposed to efforts to develop the underlying technologies, have been driven not by MITI but by Japanese industry, even in integrated circuits. The participants in the MITI-sponsored cooperative integrated circuits program went back to their own laboratories to develop the actual commercial 64K random access memory chips that have been so successful in the marketplace. Oki Electric, the fastest growing Japanese producer of 64K chips and the first Japanese company to test a 256K chip, did not even participate in the MITI program.

The Japanese government, which has played an important role in promoting its industries' fortunes through such means as protectionist trade policies, has not been a significant force in commercial technology selection and development. The successes of Japan in businesses based on advanced technology are mainly the result of smart, persistent industrial R & D management. Private corporations in Japan make long-term R & D commitments to relatively narrow areas. They pick a target, such as video recorders, assemble large teams to pursue that target, and stick with it for as long as is necessary to bring a winning product to market. They do not try to cover the R & D waterfront, and they do not back out if the payoff is not immediate. They also practice a technique that I call "innovation by experiment," whereby they put a product out on the market, even in imperfect and sometimes expensive form, and learn from the customers how to improve it. And finally, they are aggressive in acquiring, improving, and implementing technology that they did not develop.

These strategies do not explain all of Japan's success in commercial technology, but they do indicate that the real source of that success is Japanese industry. Also, they underscore the lesson that we should learn from Japan: that the selection of the product technology and its development is best left to the people intimately familiar with the technologies and the markets. Technology selection and development should not be managed from afar.

Creating Conditions for Innovation

What role should the U.S. government play with respect to R & D? That role is not to manage technology-based commercial innovation but to create the conditions for such innovation. The government should provide an encouraging and supportive environment and infrastructure within which industries select and develop commercial technology.

There are many features of such an environment that deserve attention: a favorable tax climate exemplified by R & D tax credits, by extension of those credits to software, and by fast depreciation of R & D equipment; modified antitrust laws that encourage cooperative R & D and limit damages for civil violations; export control laws and regulations that do not disrupt the interchange of scientific and technical information that is so vital to the progress of technology; and immigration laws that permit outstanding foreign scientists to remain in the United States to do R & D.

Support for University Research

The most important role for government in creating the conditions for commercial innovation is to support universities in their efforts to generate research and provide manpower. The most crucial issue we face is a lack of skilled manpower, a shortage of faculty in universities for training that manpower, and a deteriorating research capability in our great universities because of the shortages of both faculty and modern equipment for instruction and for research.

American industry today simply cannot get enough of the people it needs in such fields as microelectronics, artificial intelligence, communications, and computer science. The universities are not turning out enough R & D people in these areas, or enough research faculty. There is little that private companies can do about this. We contribute to the support of universities, but industry will never be able to meet more than a small fraction of university R & D funding needs. Even after a decade of steadily increasing industry support for universities, industry provides only about 5 percent of total university R & D funding. Congress is considering additional incentives for industry support of universities, but the fact remains that the primary responsibility for ensuring a strong, healthy academic research system and thereby for providing an adequate supply of research and skilled people must rest with the federal government.

There is wide agreement that the federal government should support the universities, and, in fact, federal basic research obligations to universities and colleges, measured in constant dollars, have grown by more than 25 percent over the past 3 years. But this is only a start in filling the needs. Department of Defense funding of basic research, for example, has only in the past 2 years returned to the level, measured in constant dollars, that it was in 1970. The Defense Department has traditionally played a vital role in supporting basic university research. A time of rapid expansion of the defense budget is no time to abandon that tradition.

Universities have had to compete with the national laboratories for the Department of Energy's research dollars. When research is funded at a university, not only does the research get done, but also students are trained, facilities are upgraded, faculty and students get more support, and thereby better faculty and students are attracted. Moreover, the students that go into industry help in the transition of advanced research into concepts for industrial innovation. When the same research is funded at a national laboratory, most of the educational dividends are lost.

Universities should not have to compete head on with national laboratories for mission agency funds. Unless the national laboratory will do a substantially better research job, the university should get the funds. The same holds for government funding of research in industry. Those funds that advocates of industrial policy propose to invest in government-directed industrial R & D would normally be much better spent in universities, unless there is a special reason why an industrial laboratory can do it much, much better.

I am not proposing that we simply throw money at universities. We need to be selective. To borrow a phrase from the industrial policy advocates, the government should stress the growth of "sunrise science and technology." Unlike the targeting of sunrise industries, the targeting of sunrise—that is, fast moving—areas of research can be done. We can identify these technologies, even if we cannot specify in advance precisely what products or industries they will generate. But we are not doing this as well as we can and should. In microelectronics, for example, a study by the Thomas Group, a Silicon Valley consulting firm, concludes that government support of university microelectronics programs totaled only about $100 million between 1980 and 1982. To put that into

tive) from that of 17 with small-cell lung carcinoma (15 positive) is striking (see Table 1). Both cancers have common ancestry, but the former is of comparatively low malignancy and the latter is extraordinarily malignant.

5) While patients with carcinoma generally showed cellular and humoral immune responses to carcinoma-associated T antigen, the humoral response was stimulated preferentially by tubular and early lobular breast carcinomas, which had T activity comparable to other carcinomas. Significantly, these carcinoma types have a favorable prognosis among breast carcinomas (*8*, *54*).

The Tn/anti-Tn system may complement the T/anti-T system in elucidating aspects of the pathogenesis of carcinoma and in early diagnosis. While the link between Tn and carcinoma has been known for a decade (*10*), this system has not been studied in the present context. Research is complicated by the usually low concentration of anti-Tn. Tn's immunodominant structure, GalNAc-α, is also the dominant part of the blood group A and Forssman haptens, which may prevent some anti-Tn immune responses. Furthermore, Tn antigen is not readily obtainable from healthy tissues (*7*). There are, however, some highly instructive experiments by nature herself that show not only how unmasked Tn arises in hematopoietic stem cells, usually persisting indefinitely without malignant change, but that Tn, the epigenetic sequela of a rare, benign, somatic mutation, occasionally precedes and then accompanies leukemia, disappears upon chemotherapy-induced remission, and reappears in relapse (*66*).

Conclusion and Prospects

The studies described here have revealed, in a large number of carcinoma patients, a close link between malignant transformation and early, persistent changes in common carcinomas: unmasked precursor antigens T and Tn, that allow the patient's immune system to qualitatively differentiate carcinoma from noncarcinoma.

On rare occasions, demonstrable T and Tn antigens occur in premalignant lesions, which may either remain that way permanently or progress to frank malignancy. Some tissues with such changes are accessible to longitudinal study and thus aid in determining the decisive point of malignant transformation. This approach may be facilitated by manipulation of immune responses, as well as by locating incipient carcinomas with labeled mono- and polyclonal anti-T and anti-Tn reagents (*25*, *26*, *67*) [but see the introduction and (*27*)]. Our monoclonal antibodies to T and Tn were generated by desialylized human O erythrocytes. We obtained three relevant specificities: anti-T, anti-Tn, as well as a specificity directed toward a moiety shared by T and Tn haptens (*67*). The three types of antibodies reacted strongly and specifically with carcinomas in immunohistochemical analyses of surgical specimens but less well in antibody absorption studies (*27*).

Our recent observation (*68*) in carcinoma patients, but not healthy persons, of a significant increase in lymphoid cell cytolytic activity against target cells with surface-exposed T and Tn antigens supports T and Tn's importance in the malignant process—especially since there was often a concomitant decrease in natural killer cell activity. The findings discussed here, although they are in an emerging phase, indicate that uncovered T and Tn antigens endow the carcinoma cells with a multitude of novel functions. These functions may be fundamental to the multistep processes of invasion and spread of carcinoma, and clearly have a profound, measurable effect on the tumor bearer's immune system. T antigen is likely to be a powerful probe in early carcinoma detection.

References and Notes

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