Future Directions for H$_x$O$_y$ Detection

NASA

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PREFACE

During the last decade, there has been considerable effort devoted to the direct measurement of the OH radical in the troposphere. Although of major importance in tropospheric photochemistry, OH is present in the troposphere at extremely low concentrations and presents an extraordinary challenge to experimentalists. A panel that reviewed a series of intercomparison ground-based and aircraft measurements in 1983 and 1984 found them to be inconclusive. The sensitivity of the OH instrumentation developed up to 1984 was felt to be inadequate to provide results that would form reliable tests of our knowledge of tropospheric photochemistry.

This workshop was held at SRI International, Menlo Park, California, August 12-15, 1985. The objective was to assess future measurement methods of the H_xO_y species that participate in tropospheric chemistry. Most of the attention in the workshop focused on OH, although HO_2 and H_2O_2 were also discussed.

The workshop participants were chosen from various parts of the scientific community. Represented were modelers of tropospheric photochemistry, experimentalists measuring H_xO_y with laser and nonlaser methods, and a group of chemists and physicists acquainted with pertinent experimental methods but not directly involved in atmospheric monitoring.

The workshop was structured to encourage free and open discussion. The participants were divided into four subpanels, each of which had members from each of the four scientific specialities. Brief talks to the entire group were alternated with discussion meetings within each of the four subpanels. Conclusions, recommendations, and ideas from the subpanels were communicated to the entire group in plenary sessions, and summary notes were made at the end of the meeting. This report on the workshop proceedings, ideas, and recommendations was compiled largely from those notes (provided by each subpanel chairperson) together with my own notes taken during the workshop.

One topic considered here is the comparison between two different measurement techniques in which averaging was taken over different temporal and/or spatial regions, and the comparison between measurements and model predictions in which different averaging was also inherent.

In this case, the report has been expanded well beyond the workshop deliberations. This issue was raised but not covered in any detail during the workshop; the ideas described here were developed mainly through discussions subsequent to the workshop. I thank Bill Chameides and particularly Jennifer Logan for many valuable conversations.

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This report has been circulated in draft form to the workshop partici-
pants, and the comments received have been incorporated into this final
version. I hope that by working from the subpanel notes I have fairly
represented all of the ideas expressed at the workshop, not just the consenses
or majority opinions; however, I am responsible for the interpretation of
these ideas.

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EXECUTIVE SUMMARY

The OH radical plays an indisputably major role in the chemistry of the troposphere. Accordingly, considerable effort has been devoted during the last decade to the development of a means for its direct detection. Such measurements are very difficult, due to the low concentration at which OH is present (of the order of 10^6 molecules per cm^3). A series of intercomparison tests were held in 1983 and 1984 for the three techniques then under development through NASA funding. The results from these tests were reviewed by an independent panel, which concluded that those methods were incapable of measuring OH reliably at the $10^6/cm^3$ level. New methods must be developed if OH concentrations are to be usefully determined in the clean troposphere.

During August of 1985, a NASA-sponsored workshop, "Future Directions for H_xO_y Detection," was held at SRI International, in Menlo Park, California. The objective of the workshop was to assess new methods for the measurement of OH radicals and to assess currently available and possible future methods for the other H_xO_y species, HO_2 and H_2O_2. The workshop participants were invited from different groups: modelers of atmospheric photochemistry, experimentalists measuring H_xO_y species with laser and nonlaser methods, and chemists and physicists familiar with such experiments but not involved in atmospheric monitoring. The workshop format consisted of brief presentations including considerable discussion, and discussions within four smaller groups. The questions asked at the workshop were broad: What are the capabilities (sensitivity, accuracy, precision, and dynamic range) needed so that the measurements furnish useful tests of tropospheric photochemistry? Can the new and proposed measurement methods meet such requirements?

There were three major conclusions from the workshop concerning the OH radical. First, it was felt that "local" measurements made by laser techniques would be ready within 2 or 3 years to furnish reliable measurements at the level of $10^6/cm^3$. Second, measurements at this level of sensitivity and with attainable levels of precision could indeed be used to make useful and interesting tests of the fast photochemistry of the troposphere. It is important, however, that the measurements be carefully designed, with respect to spatial and temporal averaging, if there is to be a meaningful comparison between results from two experimental methods or a measurement and a model. Third, nonlocal measurements using released reactants and tracers would also be very useful. These could be made on a regional or global basis, although they still require experimental design including choice of compounds.

The other H_xO_y species were not considered in the same detail as was OH. It was clear that measurement of the other species would be useful, and it appeared that there existed the capability of detecting HO_2 and H_2O_2 with the necessary sensitivity, although continued development was still necessary in each case.

More specific conclusions and recommendations are summarized.

1. For OH measurement, there are two laser-based methods, long-path absorption and low-pressure laser-induced fluorescence, that are almost ready for field testing, and a third method (two-photon laser-induced fluorescence) that should be available in 2 or 3 years. In each case, operating characteristics capable of providing meaningful tests of tropospheric photochemistry appear achievable.

2. It would be desirable to have available a nonlaser, nonspectroscopic OH method for comparison with the local laser techniques. This would probably be a regional measurement using a released chemical reactant. However, it appears that no candidate technique will be at the necessary stage of readiness within this same time frame. The search for useful reactants, to provide local and both regionally and globally averaged determinations, plus experiment design using models that include circulation, should be expanded.

3. Intercomparison among experimental determinations is crucial in order to obtain meaningful, believable measurements on OH concentrations. This intercomparison should be planned as part of the developmental effort but should be preceded by planned collaboration and open comparison among investigating teams. Results of all such tests, planned and blind, should be made public.

4. The OH molecule, with a chemical lifetime of approximately 1 sec, responds rapidly to changes in concentrations of the variables that control it. This could significantly affect comparisons among experimental determinations which average over different spatial and temporal scales, and between measurements and model predictions. The extent of such variations needs to be explored through computational experiments using the photochemical models to provide proper design of measurements including requirements for simultaneous determination of other variables.

5. Measurement of HO_2 would be very useful in our understanding of tropospheric photochemistry, and the $[OH]/[HO_2]$ ratio may be especially valuable. The most sensitive technique appears to be chemical conversion to OH, which is then detected using laser-induced fluorescence, although further development is needed.

6. A fluorometric method involving aqueous phases appears capable of measuring tropospheric H_2O_2 at useful levels of sensitivity and precision, and it has been successfully tested against diode laser absorption (which is much more species selective but less sensitive). Development of both techniques should be continued.

INTRODUCTION

The OH radical plays an indisputably major role in the chemistry of the troposphere. Reactions with OH are responsible for the removal of a wide variety of atmospheric species: CO, H_2, many hydrocarbons, H_2S, SO_2, NH_3, and several halocarbons. In the clean troposphere, OH is formed primarily via the

reaction of $O(^1D)$ with water vapor, where the oxygen is produced by photolysis of ozone by sunlight. It is removed mainly by reaction with carbon monoxide and methane. From considerations of these dominant photochemical steps, the general range of OH concentration in the clean troposphere can be estimated. It reaches maximum noontime levels of the order of 7×10^6 molecules/cm^3.

Because of the importance of this radical, considerable effort has been devoted during the last decade to the development of means for its direct measurement in the clean troposphere. It was recognized at an early date that the technique of laser-induced fluorescence (LIF) possessed in principle the necessary sensitivity to detect such a minute concentration of the radical on small enough spatial and temporal scales to constitute tests of the photochemical mechanism. In the United States, much of this developmental effort has been devoted to LIF instruments.

As progress was made and the instrumentation improved so that the detectable levels of OH dropped below 10^7/cm^3, it became apparent that there were unanticipated problems with the measurements. These problems included the generation of OH by the probing laser itself and a large background signal due to unknown fluorescing species present as a gas or aerosol. This program culminated in a series of intercomparison measurements from a ground-based station in 1983 and from an aircraft platform in 1984. The basic conclusion from those tests was that this generation of instrumentation is incapable of reliable measurements of OH at the sensitivity and precision levels needed to test the fast photochemistry of the clean troposphere. It was deemed necessary to proceed further and look to new methods for the determination of the concentration of this key radical species.

The objective of this workshop was to assess future directions for the measurement of the OH radical as well as other H_xO_y species, that is, HO_2 and H_2O_2. The questions addressed to the participants were broad: What are the capabilities (levels of sensitivity, accuracy, precision, and dynamic range) of potential measurement methods? Are measurement results that have those characteristics and limitations really useful for furthering our understanding of tropospheric photochemistry?

The major conclusions of the workshop were threefold. First, it was felt that laser-based methods now under development would be ready in 2 or 3 years to furnish reliable measurements of local OH concentration at the level of 10^6/cm^3. Second, measurements at this sensitivity and with the specified characteristics of precision, accuracy, and dynamic range would indeed form useful and interesting tests of the fast photochemistry. However, it is essential that the experiments be very carefully and properly designed in order to constitute a meaningful comparison. Third, long-term measurements of globally, seasonally averaged OH through the release of slowly reacting tracers would provide important trends over decade-long periods. Regionally averaged measurements through reactant release would also be desirable. The other H_xO_y species were not considered in the same detail as was OH. That the measurement of HO_2 would be valuable was clear, and that it too should be measurable at appropriate concentration levels appears likely with at least one method. The species H_2O_2 can be measured at the sub-ppb level with two very different methods.

In the following pages reasons for the measurement of OH and useful requirements on its precision are discussed. These discussions are followed by a description of the OH methods presented to the workshop participants, along with comments made during the workshop about each method. Considerations on HO_2 and H_2O_2 are presented after the discussion of OH techniques.

OH MEASUREMENT REQUIREMENTS FOR TESTS OF FAST PHOTOCHEMISTRY

We can at this time foresee the ability to make, within a 2- or 3-year time period, reliable measurements of the concentration of the OH radical at the $10^6/cm^3$ level. Determination of the OH concentration is not a quantity of isolated importance; rather, the value lies in using it to establish and test our overall understanding of the fast photochemistry of the troposphere. We therefore need to consider in some detail the characteristics that such measurements must possess in order for them to provide information that is interesting and useful for this purpose. In this section we discuss such considerations that are evident from current models of tropospheric photochemistry.

We think that we understand the major sources and sinks for OH in the free, clean troposphere and can calculate typical concentrations. Elementary considerations of the dominant photochemical cycles place definite constraints on the expected range of values. These are in good agreement (factors of 2 or 3) with that scant experimental information that is available. Certainly the role that OH plays as the dominant oxidation pathway for many atmospheric constituents can be considered conclusive even in the absence of further measurements. We certainly do not expect to find surprises at the level of, say, tenfold disagreement between model and measurement, a level which would suggest necessary major revisions to our understanding of the photochemistry. There is thus no urgency to develop OH measurement instrumentation simply to confirm that it is present at concentrations near $10^6/cm^3$. Rather, the issues to be addressed by measurements of the OH concentration are more subtle. They pose definite questions for and demands on both the measurement methods and the photochemical models. We address here useful levels of sensitivity, accuracy, precision, and dynamic range, the choice of appropriate experiments and measurement locales, concomitant determination of other species, and related issues.

There are two very different types of measurements of OH concentration. The first, termed globally averaged OH, represents the radical concentration averaged seasonally, diurnally, and over a large spatial region. The other, called local measurement, is made over a short time scale (minutes) and a small spatial extent, at the most, tens of km. These measurements furnish quite different though complementary constraints upon the photochemical models, and we shall discuss them separately.

Globally Averaged [OH]

Estimates of the concentration of globally averaged OH have been gauged by analysis of the budget for methyl chloroform, CH_3CCl_3 (the budgets of CH_2Cl_2, CH_2ClCH_2Cl and C_2Cl_4 have also been used for this purpose). The CH_3CCl_3 is released into the atmosphere by human activity and is removed

primarily by reaction with OH. Its chemical lifetime is long, between 5 and 10 years, so that its concentration reflects reaction with OH averaged seasonally and over the globe. Measurements of its concentration over a long period of time have been compared with model predictions, and agreement is achieved to within about a factor of 2. This difference may be ascribed to errors in the estimated release rates of the CH_3CCl_3 and uncertainties in the absolute calibration of its determination, as well as the uncertainties inherent in the model calculations of [OH].

Globally, seasonally averaged OH concentration measurements could also be made by the controlled release of known compounds that will be removed by reaction with tropospheric OH. As discussed below, there are several candidate species for such an experiment; these could also involve the simultaneous release of an inert tracer to account for transport. The design of these and related regionally averaged measurements would benefit from the application of circulation models would suggest choices of conditions and locales. Ultimately, one might hope such methods to approach absolute accuracies of the order of 10 to 20 percent and relative precision near 1 percent. As seen below, this is well beyond the accuracy or precision which would be useful for tests of the models, due to uncertainties in various input parameters. New constraints beyond the current factor of 2 are not likely to be posed by the measurement of globally averaged [OH] for some time.

Instead, the value of such experiments is most likely to come from a long-term program which measures, through some released reactant (and perhaps a coordinated tracer), changes in [OH] over a long period of time. Such trends, if observed over decades, would form an invaluable set of data. It would be complementary to long-term measurement of other minor species (e.g., CH_4, and CO), and would help place further constraints on trends in the concentrations of those species whose source terms may be difficult to quantify.

Measurements on a regional basis could also be made through the controlled release of compounds with a shorter chemical lifetime for reaction with OH. Here, the spatial scales over which the concentrations are averaged would be selected by proper choice of reaction rate and meteorological conditions.

Local [OH] Requirements

We now turn to questions of the importance of local OH measurements as tests of our understanding (through models) of the fast photochemistry of the troposphere. Because of the rapid time scale (about 1 sec) on which OH is produced and removed, it can respond to the variation in other controlling parameters. This means that OH is the only observable variable for which all the sink and source terms exist within the atmosphere itself. Its concentration thus forms a key and unique test of our understanding of that fast photochemistry. The approach begins with (the presumably available) measurements of the other important parameters, such as concentrations of O_3, H_2O, NO, CO, and CH_4, and the value of J_1, the photolysis rate for ozone. From these may be calculated local, instantaneous concentrations of OH for comparison with measurement.

By "local" measurements for OH, we must consider at the present time only laser-based techniques. Whereas it would be desirable to have a non-laser method available as well, it appears that none will be made operational in the next 3 years. In the current and proposed LIF methods, the actual volume probed has length scales of a few cm; in the long-path laser absorption, distances of the order of km are averaged. However, each such measurement involves a temporal average as well, and this aspect must be considered as part of the spatial average. In the case of the aircraft-borne LIF measurements, the typical 10 or 20 min averaging time corresponds to a spatial integration over several tens of km. For the ground-based measurements, the effective sampled volume during the time of the measurement depends on the wind velocity during the experiment. These averaging considerations have important implications concerning fluctuations in other variables during the period of the OH measurement, as will be discussed later.

When considered as a test of the photochemistry, the necessary accuracy and precision of a measurement of [OH] sensibly corresponds to, or is somewhat better than, that attainable in the model calculation itself. To make measurements of much higher accuracy or precision would not be worth the effort. To estimate the capabilities of the model calculations, consider a simple expression for the OH concentration as given by the balance between the major production and loss rates in the free, clean troposphere:

$$[OH] = \frac{k_1 J_1 [O_3] [H_2O]}{k_2 [CO] + k_3 [CH_4]} \qquad (1)$$

Here, the major removal pathways, with rate constants k_2 and k_3, respectively, are reactions with CO and CH_4. The production reaction, $O(^1D) + H_2O$, has the rate constant k_1. There exists uncertainty in knowledge of each of these rate constants and the relationship (absorption coefficient and dissociative quantum yield) of J_1 to the actual solar intensity. Values can be taken from the NASA-recommended-rate constant compilation. Considering only these errors in the input parameters to this simple model, one can quickly estimate that the uncertainty in the absolute concentration of OH is approximately the same as the concentration itself. This does not include any possible measurement uncertainties in the other variables (concentrations and solar intensity) which must be determined simultaneously. Consequently, agreement of absolute concentration between measurement and calculation is not to be sought beyond this factor of 2 at the present time.

How much better might we be able to do in the future? Again considering only the simple (but dominant) pathways expressed in Eq. (1), it is unlikely that lab measurements will reduce the aggregate uncertainty in the kinetic parameters much below 50 percent. If this is the case, one would then like to have measurements with an accuracy capability of 30 to 50 percent. With properly calibrated methods, this appears to be a limit that can be attained (but not likely much exceeded) with future instruments.

We may contrast this 30 to 50 percent level of accuracy with the value of 10 percent called for in many early OH detection planning documents. Measurements at that higher level of accuracy can probably not be achieved. It is a level at which one must seriously address questions of calibration, plus

uncertainties in fundamental parameters such as the OH absorption coefficient and enthalpy of formation. If a 10 percent level were truly necessary for any meaningful comparison with photochemical models, then attempts to measure OH concentrations would not be worthwhile. Fortunately, the apparently attainable levels of accuracy do provide useful tests of the theories.

Questions of precision and dynamic range are perhaps even more important at the present time than those of accuracy. Even in the face of inaccuracies in the available rate constants, both model and measurement should be able to follow certain changes in a single variable (e.g., $[H_2O]$) to considerably better than 50 percent, in a well-designed experiment. Precision over the time scales of such changes should be better than 30 percent to achieve meaningful comparison with the photochemical models.

With OH sensitivities at 1 to $2 \times 10^6/cm^3$, one should be able to make interesting and useful tests of the models of the fast photochemistry. These sensitivities demand signal-to-noise ratios of at least a factor of 3, corresponding to the 30 percent precision, and an absolute accuracy of a factor of 2 or better. It is not necessary to have measurements available at the $10^5/cm^3$ level to provide useful tests. The necessity for an OH instrument that is capable of operation at that sensitivity level means that one will then have reliable, routine operation at the needed 1 to $2 \times 10^6/cm^3$ level where useful tests are possible.

Under these conditions, disagreement between measurement and calculation at the factor of 3 level would likely signal a significant omission in our understanding of tropospheric photochemistry, i.e., we would suspect that some major reaction or sequence has been omitted. As noted, this seems unlikely in the free troposphere but it may be the case in a more polluted environment. At the 50-percent level of disagreement, one can begin to inquire into the need to adjust one or more of the parameters in the model as well as minor alterations in the mechanism. Measurements of sufficient precision under varying conditions may then permit the needed adjustment to be found.

We consider an example of concerns about accuracy and precision together with the need to design the testing experiments carefully. It has been suggested that not all of the OH loss rate in the clean, free troposphere can be accounted for by reaction with just CO and CH_4. Possible discrepancies of the order of 30 percent recur using the best available inputs to the models. Prime candidates for the remainder of this loss rate are nonmethane hydrocarbons including oxygenated species such as CH_3OOH. (In the clean, marine troposphere one can find regions of low nonmethane hydrocarbons but such species as methylhydroperoxide may be widespread around the globe.) Simply comparing absolute [OH] measurements with those calculated using the best model of the fast photochemistry will not answer the question of a potential 30 percent discrepancy in the loss rate, due to the inaccuracies in the rate constants as noted above. An experiment comparing a region of high CH_3OOH with one of lower value (e.g., one with more NO) could help address these issues, if the chemistry in the environment with higher NO were known well enough. This of course necessitates good concomitant determination of $[CH_3OOH]$ as well as other variables. Direct laboratory determinations of the pertinent rate constant will be of considerable value here as well.

In the relatively clean troposphere, the OH concentration is often buffered. That is, changes in the variables controlling [OH] often offset one another in their effect on this radical's concentration. For example, when NO is present at low concentrations (<5 ppt), the dominant production and loss rates are those given in Eq. (1), leading to OH typically 2 to 3 × 10^6/cm^3 for a daytime mid-latitude, spring or fall maximum. Under conditions where NO is tenfold higher, the net rate of the OH + NO_2 = HO_2 + NO reaction is reversed, and it then plays a major role in recycling the OH. Nonetheless, the OH concentration remains much the same as for very low [NO]. It would thus be of considerable value to compare measured [OH] for a variety of conditions. An example is the CH_3OOH issue discussed earlier. Here, the basic experimental issue remains precision, not accuracy, although the time scales of the experiments must be taken into account. For example, it may not be possible to make a comparison of regions of usefully varying NO_x except on different flights or very different temporal segments of the same flight. This may require maintaining that same relative precision over a long period of time. Here the experimenters must address issues of calibration: How well does the instrument remain calibrated over a given time period, and how often does one need to recalibrate to achieve the desired precision?

It was considered desirable by the workshop participants that a simple means of checking the agreement between the model and a given measurement should be devised. That is, one would wish to have some particular set of conditions in which knowledge of the photochemistry or its variation with some parameter could yield firm values for comparison with experiment. Unfortunately, consideration of the uncertainties in the kinetic parameters entering into Eq. (1) suggests that this cannot be established at a meaningful level of accuracy. Possibly, a measurement of the concentration of HO_2 simultaneously with OH under certain conditions would form such a check; however, establishing this possibility requires numerical experiments with the photochemical models.

The diurnal variation of [OH] is often exhibited as a sign of agreement between measurement and theory. The rapid response of OH to changes in its photochemical environment leads to a quick and precipitous drop in concentration upon sunset. In the clean troposphere, nighttime values of [OH] are in the neighborhood of 10^4/cm^3, well below anticipated sensitivities of next-generation instruments. (The situation is quite different in a polluted atmosphere, where reactions involving hydrocarbons can maintain the OH concentration near the 10^6 level without a photolysis source.) Because the value in the clean environment is so low, however, the nighttime disappearance of OH signal from a monitoring experiment cannot be considered agreement between model and measurement. Rather, the decrease with lack of solar flux is so well established theoretically that an experimentally observed diurnal variation must be taken merely as setting a baseline for the measurement method. Thus observation of such a diurnal variation does not constitute success for the photochemical theories, but instead furnishes the important confirmation that the detection method is not plagued by unknown background problems.

Fluctuations in Variables Controlling [OH]

In all of the proposed "local" laser-based methods, signal levels for OH are so low as to require considerable averaging time. Periods of the order of 10 min are generally considered, with 1 min being a lower limit. This is much

longer (at least a factor of 100) than the response time of OH to changes in its photochemical environment. This can have significant consequences for any comparison of monitoring results with predictions from the photochemical theories.

Clearly there is some loss of information inherent in this averaging, compared with a fully time-resolved experiment in which the OH could be observed to instantaneously respond to its photochemical environment. Such a penultimate experiment would require measurements of all variables on a 0.1 to 0.3 sec time scale, difficult if not impossible at the required sensitivity (especially OH itself). That one loses some information in the averaging is not so important as the fact that it must be taken into account for a proper quantitative comparison between model and measurement. Failure to do so could severely degrade the already limited accuracy and precision available in the comparison.

Consider Eq. (1). The instantaneous (1 sec time scale) OH production rate is determined by the product of three atmospheric variables: the concentrations of ozone and water vapor, and the photolysis rate. Suppose these were to vary together in some partially correlated way on that same 1 sec time scale. Then the average OH production rate over a 10 min measurement time scale would not be given by the product of the average of each of those variables over that time period. That is,

$$\overline{J_1 \ [O_3][H_2O]} \neq \overline{J_1} \ \overline{[O_3]} \ \overline{[H_2O]}$$

Similar considerations of course hold for the removal rate and thus for the net OH concentration measured over the longer time interval.

How does one quantitatively account for this averaging inherent in the monitoring experiments? To do so properly would require a measurement of each atmospheric variable entering into the OH calculation on the same 1 sec time scale which is the OH chemical lifetime. The kinetic model would then need to be run to compute the average OH value during the corresponding measurement period.

These questions were raised at the workshop in conjunction with the spatial averages in the long-path absorption measurements as well as the combined spatial/temporal averages found in the aircraft-borne LIF technique. They have been explored only recently in a quantitative fashion, through computational experiments performed at Georgia Institute of Technology using simple fast photochemical models. Data for the variations of O_3, CO, and H_2O were taken from CITE-I aircraft measurements (they were not performed simultaneously with OH determinations, however). These values, with about a 1-min time resolution, may be considered as exemplary changes on such a time scale. The values were then used as the input data to the model to calculate the time-dependent, instantaneous value of [OH]. This was then averaged over a 10 min time period and compared to the value of the OH concentration calculated from the averaged values of the atmospheric variables. It was found that disagreement as large as 50 percent could arise over the typical 10-min measurement period.

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Spatial and temporal variations can be equivalent depending on the measurement method. In some recent flights from the Atlantic bounday-layer experiment (ABLE), horizontal striations of O_3 were found to exist on a distance scale of a few hundred meters and were possibly present on a much smaller scale.

Another instance of such concerns can be seen in the measurements of OH and other variables in some of the KFA-Jülich long-path absorption experiments. In particular, the value of the concentration of NO_2 was measured in absorption in the visible along the same absorption path (several km in length) used for OH. During several runs, $[NO_2]$ was measured at one end of the path using a chemiluminescent sensor. The values, in the 1 to 10 ppb range, are not always in agreement. In the most extreme cases, the absorption values ranged between one-half to three times as large as those determined by chemiluminescence. One can reasonably conclude that conditions vary along the path of OH measurement and that supporting measurements made at one location are not sufficient for calculating values of [OH] for comparison.

This has important consequences for the design of an experiment and the use of its results. Comparison with any of the models of the fast photochemistry requires measurement of the other variables entering into the determination of [OH]. It is thus clear that these must be measured with rapid time response under any possible conditions where they may vary during the OH chemical lifetime. This may of course not be possible under all sets of conditions. Calculational experiments that cover a wide range of possible variation in those variables need to be performed. These experiments will give limits on the error introduced by any necessary averaging. For a given set of possible conditions, the models could be used to help assess which variables should be monitored on particular time scales and which need less attention.

Both the long-path absorption and the LIF ground-based measurements must be similarly assessed for the spatial averaging that also occurs. In the case of the long-path absorption, the quantity determined is an OH concentration averaged along that path and over the measurement period. As noted earlier, the supporting measurements of the other variables are probably impossible to determine with the same spatial variability; it is more likely that they are measured at some point near one end of the path. The choice of experimental setup may well dictate measurements in which the optical path for the laser beam is in the same direction as the wind velocity during the measurement period in order to render such averaging more tractable. Similarly, the pointwise ground-based LIF measurements must have supporting data taken over the same temporal and spatial locations. It remains important to explore possible variabilities using calculational experiments with realistic if exemplary input data.

The entire question of supporting measurements is a crucial one. At best, there exist uncertainties in other input data to the photochemical model, such as simultaneous determination of solar flux or H_2O. In many cases, average or typical values must be assumed for such variables. These can be very different from the particular values present during a measurement, even without accounting for rapid (1 sec) time variations. Unless these other variables can be simultaneously determined with good accuracy, comparison between model predictions and measurements of the OH concentration are

rendered much less precise than the factor of 2 produced by the uncertainties in the kinetic parameters. For example, measurements of H_2O have often been carried out by imprecise and unreliable humidity indicators. Needed is a reliable instrument such as the Lyman-alpha photodissociation technique that is often used in stratospheric measurements. Also, the solar flux is often simply estimated for the time of day and year and the latitude rather than taken from an actual measurement. It is simply not worthwhile to expend considerable effort on a determination of the OH concentration without supporting measurements that render a comparison with the photochemical models meaningful. Quantitative comparison with past measurements has often been rendered quite uncertain due to the lack of such supporting data; even so, it has been necessary for the modelers to proceed with comparisons, given the paucity of data of any kind. For OH to serve as the key test, the most crucial supporting data are for (attenuated) solar flux and water concentration, although other measurements would be valuable as well. For example, measurements of NO and NO_2 are not only important as input to the OH calculation but also are of value themselves. The use of piecemeal supporting measurements, that is, determining only a few variables is not cost effective.

Model Use in Experiment Design

Predictions from models of fast photochemistry in the troposphere should be considered well in advance of the ultimate comparison with experimentally determined variables, in order to properly design the experimental measurements to be made. This can occur in two identifiable ways. The first of these, discussed earlier, is to compare temporally and spatially averaged quantities with those measured under normally fluctuating conditions. The question to be addressed here is the degree of temporal and spatial resolution which must be maintained in the determination of the variables that control the test quantity, [OH]. At Georgia Institute of Technology, the modelling runs indicated that the variations in the quantities $[O_3]$ and $[H_2O]$ did affect the OH concentrations. A much larger round of computer experiments which cover a range of potential conditions will determine the precision and resolution with which those variables need be determined. The level of accuracy introduced into the measured [OH] can then be assessed. These computer experiments should address the following question: What set of supporting data (including temporal and spatial resolution) is needed to achieve meaningful comparison of [OH]? The comparisons considered are both among different measurement methods and between model predictions and a given measurement.

The other way in which the models can be used is an extension of this, in the choice of conditions and sites. At a higher level of computational experiment, these two aspects can be combined. We next consider the varying sites and conditions where OH may be determined.

A range of environments exists in which useful measurements of OH can be made. These may be classified beginning with the simplest photochemical system present in the clean, free troposphere, such as the system encountered for out over the ocean. Here, the OH concentration is determined by the local concentrations of O_3 and H_2O, which need to be measured along with the solar flux. In this system, one is far from sources of CO or CH_4. Methane may be taken safely as constant at its globally averaged value. An independent, simultaneous measurement of CO needs be made. In such an environment, NO_x

should be at a low enough level to play a minor role in the determination of the OH concentration (it should, however, also be determined to ensure it is low enough). This simple environment then forms a baseline system for a test of the major photolysis formation route and major chemical removal routes. Here, at the 30-percent OH removal-rate level, lie questions concerning the role on nonmethane hydrocarbons including methyl hydroperoxide as a possible major reactant, as noted earlier.

More promising comparisons may be possible when one compares OH concentrations measured under known variations in other conditions. The photochemical models could be used to significant advantage to help design such experiments. For example, one could conceive of a flight into a tropospheric fold, where both O_3 and NO are high, compared with the situation in the atmosphere immediately below. Another potentially useful comparison might be to fly into the plume behind the anvil of a thundercloud, where there may exist high concentrations of NO due to formation by lightning. (Here one wishes to avoid the cloud itself where heterogeneous chemistry on the water droplets may complicate the chemistry as well as the detection methods.)

Other environments that are less clean can also be the basis for OH measurements that are the basis for evaluating the understanding of OH photochemistry. In a stepwise fashion, these measurements would first be taken in locales in which moderate levels of NO_x exist, then in locales in which hydrocarbons but not NO_x are present (perhaps impossible to find), and finally in locales in which both hydrocarbons and NO_x are found to occur. In order to maintain tests of the pertinent photochemistry on any meaningful basis, however, the measurements must be made in relatively clean locales. The appropriate chemical mechanism must be limited enough that there is not a large degree of additional uncertainty introduced by errors in other rate constants.

Selection of measurement stations should involve the use of the photochemical models together with supporting data on levels of the relevant atmospheric species. As discussed below, it is desirable to first test the OH instruments themselves at a ground-based station where there exist relatively high levels of the radical. Once the measurement techniques are established, experiments can commence to test the model predictions. During this time in which the methods are established as reliable, selection of ground-based sites with proper supporting data and simple enough photochemistry can be chosen with the aid of the models. Calculations to determine the time response of supporting instruments, thus addressing the fluctuations/averaging issues, can be performed. Ultimately, one would like to select a range of environments within the troposphere, with varying amounts of NO_x and hydrocarbons. A single measurement site is too limited in the changes of environment it offers to serve as a good test of the fast photochemistry. In addition, measurement at different altitudes will be valuable: near the surface, in the boundary layer, in the free troposphere, and through the tropospause fold. Such measurements can only be performed by airplane, of course, and, in the laser-based category, they are limited at present to the LIF methods. The long-path absorption technique, offering simplicity in analysis for the OH concentration, is restricted to ground-based stations. Supporting data on other atmospheric species, plus calculations with the models, should be used to choose the sites for setting up such experiments.

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The models are also needed in the design of nonlaser determinations of [OH]. Discussed here is the use of released chemical species that react with OH on varying time scales and provide "regionally averaged" OH concentration information. The distance scales contemplated are 10s, 100s or perhaps 1000s of km in different experiments, between the local and globally averaged values. Several possible candidate molecules have been mentioned but no choices made. Here, the photochemical models as well as regional transport considerations are crucial in the choice of sites for release and measurement as well as assessment of errors introduced by averaging over several atmospheric variables. These models will be used to determine the regions over which [OH] is averaged and the need for supporting data over a regional scale. Also described herein is an experiment in which C_2D_6 is released into the troposphere at regular intervals; the objective is to determine long-term trends in globally averaged [OH]. Here, a three-dimensional global circulation model would be used to explore the expected variability and trends and to aid in the design of the experiment.

The HO_2 radical has a chemical lifetime 2 orders of magnitude longer than that of OH, i.e., about 2 min. Consequently, it does not respond as rapidly as does OH to changes in other atmospheric variables, and it forms a significantly less valuable test of fast tropospheric photochemistry. Nonetheless it was agreed that its measurement would also be valuable. Of potentially considerable interest might be the ratio, $[OH]/[HO_2]$, under certain differing atmospheric conditions. However, establishing that this ratio really is valuable requires numerical experimentation with the photochemical models.

A question also worth computational exploration concerns the averaging time needed for OH (and HO_2 as well). If OH can be measured only over a 10-min time average, does its averaged concentration over that time period yield any better information than would a measurement of the average value of HO_2 over the same period? It may not, despite the fact that the HO_2 radical does have a much longer chemical lifetime. Were HO_2 able to be measured with higher accuracy and/or precision, its measurement then could be preferable. The answer to the value of time averaged [OH] and $[HO_2]$ measurements requires performing the necessary calculations with exemplary values for fluctuating concentrations of the pertinent atmospheric variables.

OVERVIEW OF PROPOSED H_xO_y MEASUREMENT METHODS

The first portion of the workshop was spent discussing measurement requirements for the OH radical (and other H_xO_y species) indicated by needs to test models of fast tropospheric photochemistry, as detailed in the preceding sections.

A brief description of the previous measurement efforts was also given. These experiments culminated in the CITE-I flights, in which three OH measurement techniques were intercompared. They were the Ford LIF lidar, the Georgia Tech in situ LIF, and the Washington State [14]CO decay. The data from these

flights were reviewed in the summer of 1984. That assessment[1,2] led to two key conclusions. The first conclusion was that these methods were incapable of making OH concentration measurements in the clean troposphere with the necessary sensitivity and precision. The sensitivity had been outlined to the review panel as 10^6 molecules per cm^3. The more careful consideration of the real needs for testing the photochemical models described above leaves the second conclusion intact: We must proceed to a new generation of OH instruments to make such measurements on a confident, reliable, and routine basis.

During the next series of workshop sessions, a variety of measurement methods for OH, HO_2 and H_2O_2 were presented to the workshop participants for discussion and evaluation. These presentations were in the form of short written descriptions accompanied by brief (15 minute) oral presentations. In the latter, each principal investigator was requested to identify the chief technical hurdles which must be overcome for that method to operate at the projected characteristics of sensitivity and precision. The various methods were then considered by the workshop participants within the context of the measurement needs discussed earlier.

The methods discussed are here divided into three categories for discussion. The first set is the laser-based methods of measurement of OH; all of these are based on either absorption or LIF and operate on a local basis. The second group consists of chemical methods of determining OH concentrations; these can work on a global or regional basis depending on the chemical lifetime of the reacting molecule chosen. Finally, methods for determination of HO_2 and H_2O_2, which were discussed less fully during the workshop, are described.

Most of the methods presented at the workshop have been described in detail before. In particular, the report from the 1982 workshop on H_xO_y measurements[3] contains full descriptions of the laser-based methods. Included in that document are appendices on the pertinent spectroscopic and collisional dynamic considerations, plus a careful delineation of the analysis used to extract OH concentrations from the measured signals for each of the methods used in the CITE comparisons. Descriptions of the nonlaser techniques for OH determinations are also given in that report, although in considerably less detail. In many cases, the methods are also described in journal publications. Accordingly, we do not repeat here detailed descriptions of each method. The one-page summaries (which in many cases contain one or two references) are included as part of this report together with comments from the workshop participants. These shall constitute the essential description of each method for the present purpose.

In the next sections, we summarize the overall conclusions concerning H_xO_y measurement techniques.

[1] J. M. Hoell; G. L. Gregory; M. A. Carroll; M. McFarland; B. A. Ridley; D. D. Davis; J. Bradshaw; M. O. Rodgers; A. L. Torres; G. W. Sachse; G. F. Hill; E. P. Condon; R. A. Rasmussen; M. C. Campbell; J. C. Farmer; J. C. Sheppard; C. C. Wang; and L. I. Davis: "An Intercomparison of Carbon Monoxide, Nitric Oxide, and Hydroxyl Measurement Techniques: Overview of Results," J. Geophys. Res. 89, 11819-11825 (1984).

[2] Special section on GTE/CITE-I, J. Geophys. Res. 90, No. D7, 20 December 1985.

[3] J. M. Hoell, Ed., "Assessment of Techniques for Measuring Tropospheric H_xO_y," NASA Conference Publication 2332, 1984.

Overall Conclusions and Summary.- Six research groups presented methods for laser-based measurements (absorption and LIF) of the OH radical, and three groups discussed chemical means of determining its concentration.

The workshop participants reached three major conclusions concerning these methods. First, two of the laser-based techniques are fix ready for collaborative/intercomparative tests and measurements, and a third should be available in 2 or 3 years at most. In each case, the operating characteristics needed for testing fast photochemical models of the troposphere appear achievable. Second, it would be highly desirable to have a local, nonlaser-based method available for comparison. No candidate techniques, however, appear to be at the stage of readiness in the same 2- or 3-year time frame. Third, intercomparison between methods is crucial to obtaining believable, meaningful results on OH concentrations. Intercomparisons should be continued as part of the developmental effort but should be preceded by planned collaboration and comparison among the investigating teams, making measurements at the same site but not on a blind basis. In this context, it is important to make sure the methods are field worthy in ground-based operation before testing them on aircraft platforms.

Local measurements of [OH] were presented by two groups, each of which used a laser-based method. These measurements were performed in a dirty atmosphere rather than in the clean tropospheric regions in which the tests of fast photochemistry will need to take place. The long-path absorption measurements were performed in Jülich (KFA) and the low-pressure LIF measurements were performed in Portland (PSU). These results clearly indicated that each method had a potential at least close to that desired for OH measurements at the combination of sensitivity, precision, accuracy, and dynamic range which would constitute meaningful tests of the fast photochemical models in the clean troposphere. It appears that this potential should be realizable soon. Both methods should be tested at the same location when a suitable site can be chosen. This site should be a relatively clean environment but with a high enough OH concentration to be measurable.

It would be useful to have a third method available for comparison with the long-path absorption and the low-pressure methods. At this time, it appears that the only other possible candidate technique available within the next 2 or 3 years is the two-photon LIF method developed at Georgia Institute of Technology (GaT). The two-photon LIF method for OH has been demonstrated only in a laboratory environment and not yet in a field apparatus; however, its potential appears quite good.

It would be even more desirable to have available a nonlaser method for measurement of OH concentrations. An important requirement here is that such a method should be quite different from the laser-based ones. Then, agreement or disagreement could signal serious deficiencies which might be hidden in a comparison of similar methods (i.e., three all based on spectroscopic techniques). Several possible methods for determining OH by the rate of decay of various chemicals injected into the troposphere were discussed. Unfortunately, none of these appears to be at a stage at which reliable measurements can be made in the same 2- or 3-year time frame as expected for the laser-based methods. In no case has the best reactant(s) for measurement been

selected. For use as a comparison, one must very carefully understand the spatial and temporal scales covered, including the issues connected with fluctuations in other controlling variables. Here, considerable exploratory work with the chemical models needs to be performed.

The CITE intercomparisons between the Ford lidar and Georgia Institute of Technology in situ LIF methods were invaluable in establishing that neither of those two methods could perform routinely and reliably at the levels needed for testing fast photochemical models in the clean troposphere. Such inter-comparisons should be maintained as part of the OH development/measurement program, with sites carefully selected to have measurable levels of OH within the proper range for model testing. Such blind intercomparisons will constitute the only really convincing evidence that OH can be measured well at the $10^6/cm^3$ level. They should, however, be preceded by collaborative intercomparisons in which results are freely compared among the investigating teams. This sort of collaboration will uncover problems with each instrument and likely improve all of the detection methods. Ground-based testing should be thorough and complete before any aircraft-borne instrumentation is compared. In all cases, for both collaborative and blind intercomparisons, the results should be included in a report that is communicated to the scientific community by publications and conference/workshop presentations.

Laser-Based Local Measurements of OH.- In this category fall several methods as described below. At the present time two types of measurements have been reported from field tests: the KFA long-path absorption and the PSU low-pressure LIF. Results from each of these were presented at the workshop, and they provide evidence convincing to the conference participants that OH can be measured in the troposphere at concentration levels in the 1 to 10 $\times$ $10^6/cm^3$ range. Those measurements, however, were performed in environments which were significantly dirtier than the regions of the clean troposphere in which the tests of fast photochemisty must begin. It is important that both apparatuses be moved from their current respective locations to a more suitable environment. Both methods should be tested together when a suitable site can be chosen; that site should have reasonably high levels of OH and the potential for gradients in the concentration. In approximately a 2-year time frame, it is expected that the GaT two-photon LIF method will also become available for field testing and use. When it is, it should be added to the collaborative intercomparison sequence. The fact that three methods can be used for OH determination at the same time and place should yield much more confidence than the use of simply two methods. It does not appear that other laser-based methods (the Jet Propulsion Laboratory lidar, the SRI International frequency modulation absorption, or the Ford Motor Company low-pressure/fm techniques) will be ready to be added to this group within the same time frame.

These three available methods (KFA, PSU, and GaT) operate on signifi-cantly different enough principles that they can readily be taken as indepen-dent measurement techniques, even though each is laser based. In the case of the long-path absorption, the only information needed for the data analysis is knowledge of the line oscillator strengths for OH. These parameters, known to about 3 percent, are also part of the expected error in any of the spectro-scopic measurements of the radical. All of the uncertainty in the long-path absorption comes from the ease with which the absorption line can be associated with the OH radical alone, uncontaminated by interfering absorption from other species present in the measurement path. Past experiments have

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identified CH_2O and SO_2 as absorbers in this spectral region which can be present in the atmosphere in sufficient quantity to interfere with accurate measurement. However, in a cleaner environment, such as the ones that will be selected for tests of the photochemistry, these absorbers are not expected to be as much of a problem.

By contrast, the LIF-based methods require significantly more information for a prima facie data analysis or a calibration by some chemically modulated method. In both the PSU and GaT devices, such calibration methods are included. The former method uses the decay of mesitylene in a photochemical environment contained in a Teflon bag; the latter method relies on production of OH through photolysis of O_3 and reaction with H_2O, or photolysis of H_2O_2. While the chemical steps involved in each of these cycles bear further study, they appear to be reliable at a level of accuracy (perhaps 20 percent) which should be quite sufficient for the intercomparison tests. In the comparison of the Ford lidar and GaT in situ methods in CITE-I, it was found important to seek correlations between the results obtained by the two methods on the same flights. This is in contrast to seeking agreement between absolute values of [OH] in each determination. The reason is that differing calibration methods can produce different absolute values, even when each method may be determining OH in a precise manner.

Because of its dependence only on oscillator strength to determine a path-averaged [OH], the long-path absorption is often viewed as being more of a primary technique against which other techniques should be compared. There are two important caveats here: the level of interference and the averaging considerations. In the first instance, the interfering absorptions must be confidently taken into account; this appears possible in a relatively clean environment but it may be necessary to obtain simultaneous, independent determinations of the potential interfering quantities. Measurements with more than one OH line could help significantly in this regard.

Second, for purposes of intercomparison, it is crucial that the long-path absorption sample be from the same OH distribution, in space and in time, as is the LIF method. Fluctuations in quantities of the variables determining OH, as discussed, could render such a comparison meaningless by unknown but perhaps large factors. Gradients in OH along the path could render the average value of little use. Numerical experiments with the models and the consideration of appropriate meteorological information are needed to assess the actual discrepancies which can arise under typical measurement conditions. On one hand, it may turn out that appropriately comparable averages can be determined under many conditions. On the other hand, it may be that these intercomparison experiments need to be designed extremely carefully in order to avoid such problems. The answer to these questions cannot be known without computational tests.

The long-path absorption technique is clearly not applicable to aircraft measurements. For those measurements, one must use one of the LIF methods and must consider the techniques that will probably be available soon. Of the LIF methods, only a different version of the two-photon LIF method has been flight-tested; it is not known if new problems will be encountered in trying to mount the low-pressure LIF system on an airplane.

Other laser-based methods are significantly further from being field-worthy instruments than the three methods discussed thus far. These other laser-based methods include an XeCl-laser pumped lidar device (JPL), a frequency modulation absorption method (SRI), and a low-pressure LIF/fm system (Ford). The JPL experiment will depend on the existence of a very specialized (and expensive) etalon to separate the laser light scatter from the fluorescence occurring in the same (0,0) vibrational band as pumped. The frequency modulation absorption method (also pertinent to infrared measurements of other H_xO_y species) has as yet only been demonstrated at the laboratory level of 10^{-4} absorption; for actual measurements of tropospheric OH, a field instrument capable of operation at 10^{-7} detectable absorption will be necessary. The Ford concept, which includes both operation at low pressure as in the PSU system as well as frequency modulation to detect absorption in ambient OH, has also yet to be assembled as a laboratory instrument. The workshop participants encouraged continued development of these methods for OH although the current expectations are that the three aforementioned techniques (KFA, PSU, and GaT) will form the basic three intercompared methods over the next 2- or 3-year time period.

Intercomparisons and Calibration.- OH measurement instrumentation had been under development for nearly a decade preceding the CITE-I tests of 1983 and 1984. During that period, measurements of OH in the troposphere had been reported by each of the three major groups making local measurements, one from Ford (LIF lidar), one from Georgia Tech (in situ LIF), and one from Washington State (^{14}CO decay). However, no two of the three had ever been tested at the same location and same time. For the OH instrumentation, the major objective of the CITE tests was a blind intercomparison using the three methods. It was necessary to measure ambient levels of OH present at the site of and during the time of the experiments. (It should be noted that a separate intercomparison study during CITE-I was made for NO instrumentation. It showed excellent agreement among three experimental methods.)

Several difficulties were encountered during the CITE evaluation. The ground-based tests were performed at Wallops Island, Virginia, in the fall of 1983. Here, the ^{14}CO experiment failed to operate, and no statistically significant measurements were reported by the Ford lidar group. Although some measurements were reported by the Georgia Tech group, no comparison could be made with the other methods. During the flight operations, carried out in the spring of 1984, the ^{14}CO method again failed to produce any data. This time the lidar and in situ LIF methods did operate simultaneously, in eight separate daytime flights.

Due to the low levels of anticipated OH concentration, it was necessary that these data be carefully compared. The panel reviewing the data chose to look at the correlation between the results from the two LIF methods, concluding that a statistically significant correlation could not be achieved. This meant that the two LIF-based methods were not sampling OH from the same distribution, i.e., one or both were not measuring actual OH concentrations. Additionally, the signal-to-noise ratio was poor enough that neither method furnished reliable enough data to be useful for tests of tropospheric photochemistry, in the context just described. Reaching such a conclusion would not have been possible without the intercomparison study. At a given time, it is not known how much OH was present in the atmosphere within the measurement

uncertainties that existed. Only by attempting such a correlation was it possible to make the judgment that at least one of the methods was failing to detect OH. In this way the intercomparison can be considered an important success and a significant milestone in tropospheric OH detection development.

That intercomparison is a valuable part of any OH measurement program was unanimously felt by the workshop participants. Because OH cannot be provided by means of a calibrated source, together with the fact that all of the detection schemes will operate near the limits of their sensitivity, this remains the only way to ensure that each method is properly detecting a signal proportional to the actual radical concentration.

However, future OH comparisons should be carried out in a manner different from the CITE tests, in two respects. First, the instrumentation should be developed to a point where ground-based testing can be thoroughly performed before aircraft measurements are undertaken. Second, informal planned collaboration between different measurement teams should precede blind intercomparisons.

The difficulties encountered in making all the OH techniques work during the CITE tests are indicative of the complexity of this type of instrumentation. It was suggested that three different methods should be on hand for an official (blind) intercomparison performed on the ground. As noted above, those methods with the most likely potential are the low-pressure LIF, the long-path absorption, and the two-photon LIF. The fluorescence-based methods have the potential for aircraft adaptation, although tests in such a mode should not proceed until later.

A ground-based test site should be chosen on the basis of relatively high anticipated OH concentrations in the general vicinity (1 to 10 $\times$ 10^6/cm^3) of that expected in the daytime clean troposphere. Very desirable would be the potential for gradients in the OH concentration, although this may be difficult to foresee in a single ground-based location (contrasting, for example, with an aircraft flight through a thundercloud plume). Wallops Island remains a prime site due to past NASA operations there, and it should receive serious consideration. The suitability of it and other sites could be explored with the aid of photochemical models and supporting data on the concentrations of other participating species as discussed earlier.

Such tests should be planned for a long enough time period that the experimenters will be likely to encounter some range in the OH concentration. Model testing can proceed concomitantly, if the site location is clean enough to be described adequately by the theory. To do so it will be necessary to collect at the same time the pertinent supporting data (concentrations of O_3, H_2O, NO, CO, and CH_4 plus J-value) for input into the models. However, the main objective of the tests should be the comparison of the instruments, with the provision of data useful to model testing an ancillary purpose.

The comparison of the methods will serve to establish their relative precision, in the opinion of the workshop participants. The accuracy of the methods will follow subsequently; it is the precision which will indicate the important fact that OH is being measured. Any differences in absolute values between two or more successful methods are likely to point the way toward

calibration accuracy, if the signal-to-noise ratios and precision with respect to concentration gradients are each large enough.

It is important to ensure that each of the methods being intercompared is measuring the same OH concentration. These concerns have been addressed previously regarding fluctuations in correlated variables responsible for OH production and loss and measurements of those variables at the same spatial locations in each case. Here, a major question of this type may arise in comparing long-path absorption with LIF-based methods. The former operates over distance scales of the order of several km, depending on the averaging time and wind velocity (speed and direction). The latter samples distance scales directly given by wind movement of the local troposphere for a ground-base station. Are there gradients which exist in the OH concentration during a measurement period and for typical averaging times? What gradients exist in the variables controlling [OH]? The simplicity of the data analysis for the long-path absorption gives it special significance for comparison purposes, so long as it detects the same concentrations as the more local LIF-based methods. Similar considerations apply for comparison of any local chemical sensor techniques with the any laser-based methods.

To address such questions, one must perform numerical experiments with the fast photochemical models and must consider actual meteorological conditions at the chosen site.

A full, double-blind type of field comparison is the ultimate test of more than one OH detection apparatus. (In the case of OH with only its low, ambient concentration available, all of the intercomparisons are implicitly double blind in the sense that no seed compound is released.) Unless the methods to be intercompared are really ready for such an ultimate objective, these efforts can be wasted.

Consequently, informal collaborative intercomparisons should be encouraged wherever and whenever possible. Two or more different techniques would be brought to the same site for a series of measurements under either laboratory or field conditions on common atmospheric samples. The purpose is to discover at an early stage disagreements between instruments purporting to measure the same or related quantities. Most of this concept has been directed toward OH but of course it applies to other H_xO_y species when multiple measurement methods are available for them as well.

The absence of the double-blind feature in such collaborative intercomparison can lead to a concern about objectivity. Extreme care must be taken by the collaborators in order to avoid substance or appearance of "collaboration-induced agreement." However, the benefits of collaborative work outweigh such risks. Cross-fertilization will occur when groups with different areas of expertise examine others methods in a detailed and open fashion. The field of OH measurements has been characterized in the past by intense competition; a move towards cooperation could be most refreshing and productive. It is likely that more credible results and standards will emerge.

The results of the collaborative intercomparisons should be communicated to the scientific public just as blind intercomparison results are. This can take the form of journal publications, reports, and presentations at workshops

and conferences. Results of both a positive (agreement) and a negative (disagreement) nature must be reported to maintain both objectivity on the part of the investigators and credibility for the scientific community.

Over the long term, comprehensive atmospheric measurement packages capable of routinely and confidently determining concentrations of OH and other species in flight operation are desired. Achieving this objective will likely require pooling and coordination of diverse expert capabilities on a scale now foreign to the H_xO_y problem. Such collaborative intercomparison on OH is a step in this direction.

That such collaborative work should proceed prior to blind intercomparison was a nearly unanimous opinion of the workshop participants. It should be explicitly encouraged, when possible, by funding agencies; that is, it should be considered a proper, major part of a field testing program. On the other hand, it is recognized that each proposed collaboration will be a unique case in the sense of the mobility of devices, the feasibility and commonality of measurements on presumably the same samples, and the personalities of the investigators involved. Thus, clearly, support and encouragement must be tailored to the individual situations. Each of these measurement schemes and tests is itself unique enough that such choices should not be difficult.

It has been suggested in the past that some sort of OH calibration device be developed which could be used with each of the current or proposed measurement methods. This device was originally conceived as adaptable to the lidar and in situ LIF methods tested in the CITE experiments. A large volume containing OH produced in "known" quantities at the level appropriate for the clean troposphere was the basic idea. It was clear even then that developing such a device would be a major undertaking because it would need to be calibrated for the absolute OH concentration, presumably through absorption measurements. Even if, with multiple passes, path lengths of a few hundred meters could be obtained, this would limit detectable, calibrated concentrations to no less than $10^7/cm^3$ and likely much higher.

At this workshop, little attention or discussion was given to the idea of a universal OH calibration device. It is clear that the diversity of measurement techniques available for OH renders much more difficult the adaptability of any such device to the detection systems. In particular, such a calibration can really be made available only for the local measurement instrumentation, that is, LIF (including lidar). The calibration cannot be adapted for use in the long-path absorption or for most of the chemical sensor methods.

On the contrary, it was the opinion of most of the workshop participants that the OH techniques available now and in the near future are capable of operation at the proper OH levels. The LIF-based techniques that are adaptable to local calibration already include calibration procedures as part of the method. The absorption needs no calibration, only freedom from interferences. Thus an explicit intercomparison of calibration standards appeared unnecessary. In fact, it was considered quite adequate to perform an intercomparison study on ambient levels of OH, which would serve as a sufficient cross calibration.

It is of course necessary to consider quantitative aspects of the calibration methods used for each instrument. Several methods are possible for the techniques which sample the atmosphere for OH detection via LIF. The PSU group uses mesitylene (1,3,5-trimethylbenzene) decay in an air sample bag. The investigators consider this method reliable to within 10 percent although questions of complexities in the reaction scheme were raised by other participants. The GaT group used two methods: photolysis of H_2O_2 and photolysis of O_3 in the presence of H_2O. Knowledge of absolute quantum yields leads to errors of perhaps 30 percent in derived absolute [OH]. Comfortingly, the agreement in the OH produced by each method agrees to within about 20 percent for the worst case, under varying conditions such that the [OH] changed by a factor of 30 over the entire range. Other methods that have been suggested are the production of OH by the chemical reactions $H + NO_2$ and $F + H_2O$.

A more careful quantitative consideration of the errors inherent in any of these schemes needs to be undertaken, perhaps augmented by further laboratory studies on the reaction sequences themselves.

Chemical Sensors for Local OH.- Chemical methods have the potential to provide different and at times very complementary information on OH concentrations, compared to the laser techniques. The development of reactive compounds with the correct chemical properties seems to be the chief stumbling block. Work should be encouraged along these lines. A wide variety of time scales may be available from global measurements (averaging over years) to local, short-term chemical releases. The short-term methods need supporting development along the lines of kinetic and mechanistic information. The value of release of multiple samples was noted.

The OH concentration on a globally averaged basis has been measured to within about a factor of 2 by considerations of the concentration of methyl chloroform and other halocarbons. Here, the known reaction rate and the best estimated release rate can be combined to give [OH]. Instead of using reactive tracers on such an opportunistic basis, they can be released purposely into the atmosphere. A method for such a global average is described in the next section. We here consider measurements on a more local or regional basis.

One technique, which has been performed by a team at Washington State, is the radioactive CO decay rate measurement. Experiments using this technique rely on a sensitive measurement; at 10^6 OH, less than 0.1 percent of the CO is converted in a 1-hr residence time. Early measurements in ground-based stations around the globe gave results with extremely nice signal-to-noise ratios. However, attempts to make the system operate in either the ground-based or aircraft-based CITE measurements were unsuccessful; in no segment of either mission did the system operate at a level in which signal could be detected. In spite of its early promise, this method received no attention by any investigator during the workshop. The conclusions which we should reach concerning the ^{14}CO experiments of Washington State during CITE-I are not clear. It would be useful for this matter to be examined further by those particular workshop participants who are familiar with chemical release methods.

Rather, techniques involving the decay of specific compounds that could be injected into the atmosphere were considered. Many of the suggestions included one or more man-made halogenated species. Depending on reaction time and wind conditions, these techniques could, in principle, be tailor-made to cover particular distance scales, such as those from a few km to perhaps a thousand km in distance, before reacting. In order to compensate for the transport itself, an inert tracer (one with a much longer chemical lifetime) would also be released at the same time. A release along a chain of islands might provide the environment to employ chemical sensors over a scale of hundreds of kilometers in the clean marine troposphere.

It is extremely desirable to have a different method available than the spectroscopically based technique for local OH measurement. The use of a chemical sensor for OH would be subject to a very different set of potential systematic errors. The ability to establish agreement (or discover a lack of agreement) with one or more of the laser-based methods would be very important in establishing the validity of local OH measurements. If only for this reason, the development of a method to chemically determine local [OH] should receive high priority. However, in contrast to the situation that there are laser-based systems now operating and others in the proposal and/or early development stage, there exist few efforts that seek to establish a chemical sensor technique. This search should be expanded.

Several molecules have been suggested for use in the chemical sensor technique (as described in the sections on each technique). It would be best, of course, to choose a compound for which there is no natural source or possibility of contamination from an uncontrolled release of the specific reactant. The choice of compounds is not necessarily confined to the simple consideration of only these aspects together with some given chemical lifetime versus OH. One also needs to consider the mechanism of reaction, that is, the reaction with unsaturated molecules which can proceed via adduct formation may have a complex combined temperature/pressure dependence. The photochemistry of the chosen compound and the possibility of reaction with other species must of course be taken into account. A key criterion is the choice of some molecule with a specific detection signature because it will be necessary to measure changes in a relatively small quantity. Addition of too much of the reactant may perturb the chemistry in the region being sampled.

Accuracies of the order of 1 percent are realistic. It is important to keep in mind the chemistry of the released compounds, however. What do they themselves measure and do they perturb the chemistry controlling OH, were two questions raised by several speakers. The combined temperature and pressure dependence of reaction rate constants of OH with unsaturated hydrocarbons needs to be kept in mind.

It is important to consider the chemical sensors and the laser-based techniques with respect to the ability to intercompare them. It is attractive to consider that the same quantity, the OH concentration, could be measured by two very different types of methods as a very unique test of each system. However, we must ask exactly how the same quantity is being sampled. Only a chemical sensor which acquires samples from the same very local region as that covered by the local LIF methods can be compared directly. Here one finds the same concerns which accompanied the discussion of comparison of the long-path absorption and LIF methods. In the case of chemical sensors, the differences

(and abilities to compare quantitatively) diminish with the distance scale covered by the chemical methods. Fluctuations in the variables determining OH can easily render improper any such comparison if too great a time and distance are averaged over. The merits of each proposed measurement must be considered, using the tropospheric models to assess the potential levels of disagreement necessarily built in by the averaging. Of course, these considerations apply only to the intercomparison and not to the inherent value of the chemical sensors in providing data useful as tests of the models, with calculations properly configured to average over the same variables as in the experiments.

Long-Term Globally Averaged OH.- A proposed measurement of globally averaged OH over a long-term period received considerable (though not universal) attention and enthusiasm at the workshop. The proposal itself concerned the release of deuterated ethane in known amounts and measurements of its globally uniform concentrations at various locations. Mass spectroscopic analyses should furnish accuracies of 1 to 3 percent.

Determinations of globally, seasonally averaged OH concentrations would emerge from these measurements. The level of measurement accuracy attainable is well beyond that needed for direct comparison of this average quantity with that calculated from models. In fact, the agreement to within a factor of 2 found by comparison with the methyl chloroform data is about as good as can be expected, given the uncertainties in the kinetic parameters used as input to the models. Consequently, simply as an immediate test of an understanding of the photochemistry, this experiment has little value.

What is most appealing about this method, however, is the possibility of providing information on the change in the globally, seasonally averaged OH concentrations over a long period of time, say 50 or more years. With measurement accuracy in the C_2D_6 concentration of 1 to 3 percent, the relative change in OH concentration would be followed to the same level of precision. This would permit small changes in the OH concentration to be followed over the long term, if these measurements are repeated every 5 or 10 years. For example, recent calculations considering worldwide methane concentrations indicate that [OH] has decreased 25 percent between 1950 (when $[CH_4]$ = 1.14 ppm) and the present ($[CH_4]$ = 1.65 ppm). This result relies on assumptions such as that the concentrations of NO_x and O_3 were the same in 1950 as today.

With concurrent measurements of other variables, long-term trends in [OH] concentration could provide the key evidence for understanding and ultimately forecasting long-term effects on concentrations of O_3 molecular species involved in the greenhouse effect. One of the workshop participants felt that this long-term [OH] determination was the most important global tropospheric variable that we could measure. Many of the other participants, though less extreme in their enthusiasm, agreed that such a measurement was very worthwhile.

On the other hand, several participants strongly questioned this experiment altogether. Their objection was that repeatable measurements could not be made at the necessary level of precision. If the deuterated ethane were released uniformly around the globe, its concentration after a year would vary about 15 percent depending on seasonal and spatial inhomogeneities and circulation; that is, measurements repeated later would be good to only that

amount and would be inadequate to produce the desired long-term trends. The consensus was that, in some form, such a measurement should be supported and commence as rapidly as it can be properly designed.

The compound C_2D_6 was selected as a prime candidate molecule because it is unlikely that this compound would be released into the atmosphere except in this experiment. It was also selected based on a consideration of appropriate reaction times and detection limits using mass spectroscopy. There are several potential disadvantages that must be explored. One estimate is that about 20 percent of the disappearance rate of the C_2D_6 globally will be caused by reaction with $C\ell$ atoms, although other participants questioned that there is enough $C\ell$ in the troposphere to cause any removal.

Further, all participants agreed that uncertainties can be caused by nonuniformities in concentration due to patterns in release sites and sampling locations, folded together with a time-varying OH concentration distribution on a large scale. It is known, for example, that C_2H_6 concentrations vary seasonally by a factor of 3 at given sampling stations. One must consider the relationship of the measured concentration (at a given point in space and time) to that considered to be the average for obtaining long-term trends in [OH].

Again it is necessary for further experiment design to proceed with the aid of models of the pertinent photochemistry of the troposphere, including global circulation models. Ultimately, of course, one must relate the measured quantities to those that are meaningful for model comparisons; this will require careful selection of release and sampling patterns, with attention paid to errors introduced by assumptions as to nonuniform circulation. It is possible that other molecules (such as $CD_3CF_2CD_3$, which is less common than C_2D_6) or multiple species might be released to check for effects of nonuniformity in circulation. In any case, folding in the OH concentration distribution through model calculations will be necessary.

Measurement Techniques for HO_2 and H_2O_2

Considerably less attention was paid to these species than to OH. Part of the reason is the special importance attached to OH as a test of the understanding of fast photochemistry of the troposphere, and part is the attention already paid to development of OH instrumentation over the last decade.

HO_2 has a chemical lifetime of the order of 100 sec in the free, clean troposphere and is present in typical quantities of the order of 10^8 molecules/cm^3. This longer reaction time means that it is not as good a test of the fast photochemical models as is OH, but its measurement would nonetheless form an important and useful quantity. Of particular interest may be the ratio, $[OH]/[HO_2]$. Further, as discussed in the section on needs for testing the models, fluctuations in other variables over the time period of the measurement could render the HO_2 concentration as meaningful as that of OH under certain circumstances; answers to these questions can only be gained by computational experiments.

Thus it is worthwhile to seek reliable, sensitive measurements of HO_2 as well as OH. Three suggestions were made. One suggestion is to use a chemical

sensor that depends on reaction with NO in the presence of excess CO. This instrument responds to total peroxy radicals, that is, RO_2 as well as HO_2. However, each radical is differently weighted so the result is not a linear sum of all peroxy species. It appears to work reliably and cheaply, although for operation in the field, ambient NO_2 concentrations will limit the overall peroxy sensitivity to about 10^8. This chemical sensor can provide interesting, useful numbers which must constrain the photochemical models within certain limits. However, it appears that tests of those models at a level of accuracy corresponding to uncertainties in the input kinetic data will require more specificity between HO_2 and other peroxy radicals.

Another HO_2 instrument determines the concentration by chemical conversion (reaction with NO) to the OH radical, which is then detected with low-pressure LIF. The ultimate sensitivity expected is in the 10^7 range, yielding good precision for anticipated clean tropospheric concentrations. The concern here is one of interference; present measurements show discrepancies of factors of 2 although it is expected that eventually these can be accounted for.

The third method is that of tunable-diode laser absorption in a multipass arrangement. In this method, measurement of HO_2 is marginal at 10^8 molecules per cm^3, so that in the present configuration the diode laser approach does not appear sensitive enough to yield measurements of the needed precision for tests of clean tropospheric photochemistry. However, the possibility of future improvements, in particular the addition of frequency modulation, could likely improve this limit considerably.

An additional method for detecting HO_2 was not discussed at the meeting. This method is a matrix trapping/electron spin resonance method used at KFA. Preliminary results reported at the workshop indicate sensitivities at the level of 10^8 HO_2 molecules/cm^3 in the atmosphere, at the margin of utility for tests of the photochemistry. However, in regions of high concentration of the hydrogen peroxide, this could serve as a useful method for intercomparison. It was suggested that the PSU LIF, the Denver chemical amplification, and the KFA ESR methods be tested together in the same comparative way as envisioned for OH techniques. Development of a plan and protocol for such a comparison should be encouraged. When comparison issues are considered, it is important to consider spatial and temporal averages as for OH. With a longer chemical lifetime, different levels of fluctuation in controlling variables can be tolerated.

There are two very different techniques available for H_2O_2. These are a fluorometric method in which the sample is brought into an aqueous phase in which the peroxide reacts with compounds that produce chemiluminescence. Interferences from commonly found atmospheric species (e.g., O_3 and SO_2) do not appear to be a problem, but that question warrants further study in both the laboratory and the field. The detection limit is quoted as better than 50 ppt, which would yield a signal-to-noise ratio of about 10 for concentrations expected for H_2O_2 in the clean troposphere.

The other method for determination of H_2O_2 is the diode laser absorption. This method has the advantage of being very specific for the species measured, but its sensitivity is lower. In a 1- to 10-min averaging time, concentrations of about 300 ppt can be detected; this is not as low as is

desirable. With a longer multipass cell, sensitivities <100 ppt are projected. The possiblity of adding frequency modulation may lower this yet further.

Importantly, it was reported at the workshop that the diode laser and the fluorometric method have been tested together in regions of high H_2O_2 (3 to 5 ppb) and have been found to give good agreement, although the details of that comparison are not yet available. This is a case of seeking a comparison between two very different kinds of techniques that involve quite different potential systematic errors.

Laboratory Support Studies

The analytical technologies used in these detection schemes had their birth in physics and chemistry laboratories that concentrated on the fundamental aspects of molecular behavior not on the detection methods themselves. However, now that the H_xO_y instruments are maturing, the laboratory efforts must aim at suppporting and filling identified and probable data gaps. These laboratory studies can be used to enhance the utility of and confidence in the methods now in use and to help provide for the next generation of detection technologies. Four specific areas were identified during the workshop as needing additional research. They are briefly discussed.

Chemical Conversion Methodology.- Two current methods use the chemical conversion of HO_2 and/or RO_2 to other chemical species in order to measure the concentrations of these peroxy radicals. The accuracy of the technique is directly dependent on the quantitative understanding of the chemistry of these conversion steps. It must be known how changes in environmental conditions such as pressure, temperature, and concentrations of other species (including water vapor) affect the conversion. A specific area of direct and immediate concern here was HO_2 conversion to OH by high levels of NO, under conditions where there exists a potential for formation of NO_3 and reactions of RO_2 to regenerate OH and/or HO_2.

Calibration Systems for OH-HO_2.- Presently there is a reasonable diversity of calibration techniques for the generation of OH radicals. The good agreement between H_2O_2 photolysis and O_3 photolysis calibrations suggests no serious systematic errors in the parameters used to calculate the absolute concentration of OH generated. Nonetheless, further laboratory study to quantify the error limits in these processes is valuable. The PSU method of mesitylene decay in an air sample deserves further attention to quantify errors introduced by possible adduct formation and reaction on the sample container walls.

By contrast, methods for calibration of HO_2 appear to have significant gaps. The PSU study used two methods: HO_2 decay and photolysis of NO-CH_2O mixtures; the results were found to differ by a factor of 2. Since the HO_2 coupling reaction is important in the calibration and chemistry of the HO_2 systems, a careful examination should be made of the rate constant. It would appear that a calibration system for this species requires significantly more work.

Fundamental Spectroscopic and Dynamic Studies on OH.- All of the laser-based OH methods depend to some degree on knowledge of fundamental parameters of behavior of the excited and ground states of OH. Absorption coefficients, needed for the long-path absorption, appear in good shape at a 3-percent level of accuracy. The LIF methods also require knowledge of certain collisional energy transfer rates. Needed here are quenching rate constants for the electronically excited state which have recently been found to vary significantly with temperature over the range encountered for tropospheric monitoring. This means that even systems calibrated for OH will need this correction factor for changes in quantum yield as a function of local temperature. The PSU experiment will require similar information on vibrational energy transfer in the excited state, and the JPL lidar experiments need data concerning rotational energy transfer. The GaT two photon method requires, in addition to the aforementioned items, laboratory studies of energy transfer in the ground electronic state among rotational, spin-orbit, λ-doublet, and orientational quantum levels.

These fundamental studies should not be limited to just these physical parameters but should be flexible and expansive enough to incorporate new needs and set the base for future generations of detection instrumentation.

Chemiluminescent Sensors.- One idea raised during the workshop was the possibility of developing a cheap, portable and reliable chemiluminescent sensor for OH in comparison to the complex laser instrumentation now in use. No distinct ideas were offered although the idea appeared worth exploring. At the very low levels at which [OH] is present, a prime concern is the lack of specificity resulting from interferences associated with reactions with more abundant species. Developing concepts along these lines is to be encouraged.

Two Questions: The Cost of Cheap Experiments and the Penultimate OH Machine?

Two further questions were raised but not discussed during the workshop. The first concerned comments which surrounded the discussion of comparisons between nearly every potential laser and nonlaser method. Here, laser experiments with their clearly visible, large amounts of complex hardware were labelled expensive, in contrast to nonlaser experiments that chemical sampling, as in the fluorometric H_2O_2 determinations. The development of a "cheap" chemiluminescent sensor for OH was asked for.

Are nonlaser experiments actually cheap? The real question concerns the fraction of actual cost represented by the capital investment in hardware. Other costs may well be the same, depending on the number of person-years involved in each measurement sequence. A proper cost comparison would also take into account the budget spent on flight or ground station operations devoted to the measurement in question.

This question of comparative costs is one which should be looked at by agency personnel with access to the correct budgetary figures. It is necessary information if funding decisions are to include as a criterion the cost of a given measurement method.

A second question that was raised will eventually need attention at a level high in the tropospheric measurement programs. This question concerns measurement techniques, each of which sample OH on the same spatial and temporal scales, e.g., the PSU low-pressure LIF and the GaT 2-photon LIF instruments. The question is: Should we direct our attention to the development of a single, penultimate OH device which has all the desired characteristics? Or, should we maintain, for a long period of time, development and use of more than one method, so that we have the ability to intercompare them for a variety of atmospheric conditions? There are advantages and disadvantages in each choice. By the time the performance of the next generation of OH devices can be demonstrated, that is, within 2 or 3 years, this question should be a topic of concern and discussion among both scientists and funding agency personnel involved in tropospheric chemistry.

APPENDIX

ABSTRACTS AND COMMENTS ON SPECIFIC MEASUREMENT METHODS

Abstracts of each H_xO_y measurement method that was presented to the workshop are given in this appendix. A comments section is included which summarizes discussions and questions raised by the workshop participants during both the smaller panel meetings and the open discussions with the entire group.

This section assumes familiarity with each method at a level corresponding to the references given in the abstracts.

OH RADICAL MEASUREMENTS BY OPTICAL ABSORPTION SPECTROSCOPY

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The long-path absorption spectroscopy (LPA) measurement of OH utilizes the strong UV absorption spectrum of the molecule with well-resolved rotational lines around 308 nm. The OH lines $Q_1(2)$ and $Q_{21}(2)$ of the $A^2\Sigma^+$, $v'=0$ <-- $X^2\pi_{3/2}$, $v''=0$ transition were selected for the detection of OH.

The light source consists of an Ar^+ ion laser pumped CW dye laser, the output of which is frequency doubled to emit a spectrally smooth light profile of 0.1 nm FWHM at 308 nm. This is considerably broader than the sharp (0.0018nm wide) absorption features of OH and also wider than the total spectral region (0.06 nm) scanned around the OH lines.

For field measurements a Cassegrain-type telescope expands the small diameter of the original laser beam by a factor of 50 to about a 0.25-m diameter in order to reduce the divergence of the beam as well as its mean photon flux density, thus reducing the maximum self-generated OH concentration to $<4*10^4$ cm^{-3}. The light is passed into the open atmosphere and reflected at about 5 km distance resulting in a 10-km light path length. A telescope focuses the returning light onto the entrance slit of a monochromator the single exit slit of which is replaced by a mechanical scanning device operating at a scan repetition rate of 6.6 KHz. For a typical measurement (1h duration) some $2*10^7$ scans are averaged, rendering the contribution of atmospheric turbulence to the spectral noise negligible.

Noise and detection limit: Ideally, the noise should be limited by photon associated noise being proportional to $(1/N)^{0.5}$ (N total number of photons received per wavelength interval and measuring period) However, due to laser-generated noise the level actually observed is up to one order of magnitude higher than this expectation.

For a given system noise level the sensitivity could be improved by using longer light paths, because the absorption signal is proportional to the pathlength while the system noise remains constant. However, the length of the lightpath can only be extended until the photon associated noise becomes the limiting factor. Moreover, with very long lightpaths the occasions for the OH measurement are reduced to exceptionally clear days. At a practical optimum of 10 km light path length a detection limit of $5*10^5$ OH cm^{-3} has been reached [Hübler et al. 1984].

Interferences: Of the several possible sources of interference with the atmospheric OH signal (solar stray light, OH radicals produced by the laser UV radiation, and narrow band (<.005 nm) absorption features of other atmospheric species overlapping the

OH absorption lines) only the latter has been found to be noticeable. Absorption features due to SO_2, CH_2O and CS_2 could interfere, fortunately their superimposed spectra can be quantitatively deconvoluted, since the spectral interval contains enough significant information to unambiguously identify those absorption features, (if the gases are present in sufficient concentrations). Since known absorption features can be eliminated from the spectra 10^6 OH cm^{-3} would just be detectable in the presence of 22 ppb SO_2 or 120 ppb CH_2O.

Presently efforts are made to increase the sensitivity of the detection by higher UV power and through better quality (spectrally smoother) laser light. Also photodiode arrays will replace the mechanical scanning technique leading to a much better light utilization due to their multiplex advantage.

Hübler, G., D. Perner, U. Platt, A. Toennissen, and D.H. Ehhalt, Groundlevel OH Radical Concentration: New Measurements by Optical Absorption, J. Geophys. Res., 89, 1309-1319, 1984

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OH MEASUREMENT BY LASER LIGHT ABSORPTION

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Since the first attempt to measure atmospheric hydroxyl radicals by optical absorption in 1975 (Perner et al., 1976) this method has been continuously developed further and its major obstacles and limitations are known today (Huebler et al., 1984). Three groups in Germany at Juelich, Frankfurt and Goettingen use the long-path absorption method and a fourth experiment is being built at the Max-Planck Institut in Mainz and a number of points have to be considered.

1 The laser beam needs to be expanded in order to reduce the beam divergence. At the same time the energy density of the laser beam which produces OH via ozone photolysis is reduced to such an extent that the self-produced OH concentration ranges well below the atmospheric value.
2 Atmospheric absorptions should be observed over a wide spectral range (40 cm^{-1}) so that not only the OH radicals are properly identified by several rotational lines but their absorption can be corrected for interfering absorptions from other air constituents as SO_2, CH_2O, CS_2, etc. which can be identified in a wide spectral range with more confidence.
3 Air turbulence demands fast (within about 100 µs) spectral scanning or probing on and off the absorption line.
4 Energy requirements should be kept small in field operations.

In the experiment frequency doubled dye laser pulses at 308 nm are produced. The picosecond light pulses are expected to show a smooth profile (light intensity against wavelength) which will be broadened to the required spectral width according to the uncertainty principle. The pump laser will be an optoacoustically modulated Nd:YAG laser.

After its path through the atmosphere the light is dispersed by a spectrograph of 0.1 cm^{-1} resolution and simultaneously collected by the 1024 channels of a photodiode array. According to a calculation based on the level of light seen by the detector a sensitivity of 105 molecules OH cm^{-3} along a 10-km path is expected for 2 minutes integration time.

Perner, D., D.H. Ehhalt, H.W. Paetz, U. Platt, E.P. Roeth and A. Volz, OH-radicals in the lower troposphere, Geophys. Res. Lett., 3, 466-468, 1976.

Huebler, G., D. Perner, U. Platt, A. Toenissen, and D. Ehhalt, Groundlevel OH radical concentration: New measurements by optical absorption, J. Geophys. Res., 89, 1309-1319, 1984.

Comments

These two variants on long-path absorption, to be developed at Mainz and Jülich, were both presented by Platt; the comments were directed at long-path absorption in general.

Platt estimated that contributions to the accuracy were 10 percent from systematic errors and 25 percent from the signal-to-noise ratio. It was felt that this method should be moved out of Jülich as soon as possible and into an environment which is neither dirty nor a desert (that is, where one can gain some understanding of the [OH] in a clean region which does contain the radical). The long-path absorption was viewed by most of the workshop participants as a primary check, not subject to serious systematic errors. Not discussed at the workshop, however, were the concerns about averaging [OH] and the other controlling variables and their influence upon comparison with models and other measurement results.

The $Q_1 1$ line is used for the measurement because it is the strongest; the interferences due to CH_2O and SO_2 are about the same for all strong lines. Some of the panelists felt that an effort should be made to consider determining a correlation among multiple peaks to avoid the interferences.

The rapid-scan method at Jülich is designed to avoid atmospheric turbulence; noise (variations in the spectral/temporal mode patterns) in the laser has not been considered. Also at Jülich, a low-pressure sampling cell measurement of [OH] is beginning. This is similar to the Portland State technique, although 308 nm excitation will be employed and gain-switching time-gating will be used.

TROPOSPHERIC HO DETERMINATION BY FAGE

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In the detection of tropospheric HO by laser-excited fluorescence, we have introduced an alternative air-sampling method, named FAGE (Fluorescence Assay with Gas Expansion). Here the air is expanded through a nozzle (to 10^{-2}-10^{-3} atm) prior to excitation, in order to improve the ratio of the HO signal to the scattered, fluorescent, and photolytic backgrounds. The improvement comes from the differing pressure dependence of the intensities of these four terms, as well as the distinguishability of their temporal waveforms at low pressures when excited by a pulsed laser.

In this work, HO has been excited by a YAG/dye laser via the A,1 <-- X,0 $Q_1 1,1'$ transitions at 282 nm, with fluorescence detection in the A,0 -->, X,0 band near 309 nm. Other lasers and pumping paths may perform as well or better in this method. We have determined HO in urban air, where all three background terms are larger than in the remote troposphere.

With FAGE, chemical modulation of the HO signal has been achieved by hydrocarbon addition to the nozzle flow, converting photolytic HO from an interference to a background. Chemical calibration of the instrumental response to external HO has also been achieved, by hydrocarbon decay, at HO concentrations within the ambient range.

The method and the instrument have been described in Reference 1. Since then, FAGE sensitivity to ambient HO has been improved by a higher rep-rate, higher pulse-energy laser; narrowband interference filters with f/1.5 collectors; and two parallel air-sampling channels. A steady-state modification of the hydrocarbon-decay method has allowed multipoint FAGE calibration throughout the NO-NO_2-O_3 progression.

Reference 1:

    T.M. Hard, R.J. O'Brien, C.Y. Chan and A.A. Mehrabzadeh, Environmental Science and Technology 18 768-777 (1984).

Comments

These authors claim a 10 percent absolute accuracy using their method of sampling from a Teflon bag containing OH and other species. In the future, with optimization of the pressure reduction nozzle and time gating, they expect to measure $2 \times 10^5/cm^3$, with a signal-to-noise level of 2 and an absolute accuracy within a factor of 2.

The OH level in the bag is calibrated by the time decay of hydrocarbons and the FAGE technique by sampling from the bag. Questions were raised concerning wall effects, but these only occur near the end of collapse of the bag. The probe is moved around within the bag itself. The photochemical conditions which produce the OH are varied; these are concentrations of O_3, H_2O, NO and hydrocarbon, and the ultraviolet intensity. What are the effects from unsaturated compounds, which have a pressure and temperature dependent rate constant? Altogether, considerable concern was voiced by the workshop participants about the calibration method; while there were no obvious problems, it was felt that a study of the method was warranted.

This method appears ready to move into a ground-based collaborative effort together with the long-path absorption. Consideration has not yet been given to aircraft operation and special problems which could occur there, for example, H_2O clustering at 220K for flights higher in the troposphere.

This method can be combined directly with a determination of HO_2 by chemical conversion as described below. This combination has decided appeal for measurements of the ratio $[OH]/[HO_2]$ which appears of special interest as a test of the models.

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TWO-PHOTON LASER-INDUCED FLUORESCENCE DETECTION OF OH

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The TP-LIF OH sensor is based on the principle that a molecule having multiple energy states, all of which are bonding, can be pumped into the highest state with the resulting fluorescence being blue-shifted relative to all pumping wavelengths. In this way, one can successfully discriminate against virtually all noise sources in the system using long wavelength blocking filters in conjunction with solar-blind photomultiplier tubes. Thus, these systems tend to be "signal limited" rather than "signal-to-noise limited" as is true of the SP-LIF technique as well as other conventional analytical methods. The trick to achieving the above sampling scheme, with high efficiency, is in the use of high photon fluxes of short time duration. Obviously, the latter type of light source is fulfilled nicely by available pulsed lasers. From an operational point of view, however, this laser source needs to be tunable. The latter characteristic permits extremely high selectivity for the detection of a diatomic or simple polyatomic molecule by taking advantage of the high-resolution spectroscopic features of these type species.

The Georgia Tech group has now applied this multi-photon LIF detection scheme to several chemical systems including: NO, Hg, I_2, and OH. The most extensively developed system is that involving the detection of NO. This TP-LIF system has undergone both extensive ground-based and airborne field testing.

The current TP-LIF OH system exists in prototype form only; even so, it has enabled us to carry out proof-of-concept tests and in addition has permitted a realistic appraisal of two of the major questions related to the LIF detection of OH: (1) UV laser generated OH interference; and (2) non-resonance fluorescence background noise.

The prototype TP-LIF OH system is based on the sequential pumping of OH from $^2\Pi$, v"=0 to $^2\Pi$, v"=1 or 2 followed by electronic pumping of the $^2\Pi$ (v"=1 or 2) state to $^2\Sigma$(v'=0 or 1). The shortest pumping wavelength required in either of these schemes is ~ 347 nm whereas fluorescence occurs at ~ 309 nm. Based on the results derived from the prototype system, projected detection limits for OH under tropospheric conditions range from the low 10^4 to the low 10^5 molecules/cm^3 for a 10-minute integration time. The major requirement in moving the existing prototype system to the above stated level of performance is the availability of a high-energy IR pulsed laser centered at ~ 1.4 or 2.8μm. A discussion of possible future IR laser sources which will meet our requirements as well as other operational characteristics of the TP-LIF OH system will be presented during the H_xO_y workshop.

Comments

The two-photon method of detection of OH has been demonstrated only in a laboratory instrument although, these investigators stress, two-photon detection hardware for NO has proved flight worthy. This was thought of by most of the participants as a valuable third technique, behind the long-path absorption and reduced pressure methods, which would be ready in 2 or 3 years.

A major question raised was the ease with which the required pulse energy (200 mJ per pulse) in the infrared could be generated. There are several possibilities, all yet to be evaluated: (i) A titanium-sapphire tunable laser, Stokes-shifted twice in H_2; this will require 1 to 1.5 years development; (ii) An efficient infrared dye pumped by Nd:YAG 1.064 μm radiation, which has been demonstrated in Japan and the dye delivered to Georgia Institute of Technology; within a year it should be known how well this can be operated; and (iii) An I_2 laser which, when Stokes-shifted once, may have a coincidental overlap with an OH line; borrowed from the manufacturer, this possibility can be checked within the year.

Interference levels are quite low using this method. At 60 ppb, the O_3-H_2O laser-created OH will cause background signals equivalent to <5000 OH per cm^3. Photolysis of HNO_3 at 100 ppt yields OH signals of $70/cm^3$, and that of H_2O_2 at 1 ppb gives an OH signal of $10/cm^3$. This group estimates an overall calibration accuracy of 20 percent, deduced from an examination of the methods (H_2O_2 and O_3-H_2O photolysis) in the CITE-I evaluation. With 1 to 10 minutes averaging time, an overall accuracy within a factor of 1.5 is expected, with detectable limits lower than $10^5/cm^3$ at a signal-to-noise level of unity.

OH DETECTION BY FORD MOTOR COMPANY

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Dearborn, Michigan

Dr. Wang presented two different methods for detection of OH: a low-pressure flow cell system and a frequency modulation absorption measurement. He did not provide the requested one-page description of each method, and this description is taken from D. R. Crosley's notes during Wang's talk.

Using conventional absorption spectroscopy, Wang quoted detection limits of 10^6 OH molecules per cm^3 using a 30-minute averaging time on the ground, and a 3-hour averaging time in the air for present apparatus in use at Ford. With the addition of FM spectroscopy at 1 GHz, a double-beam machine should permit detectable absorption of 10^{-7} and an OH limit of 10^5 per cm^3 in a 30-minute averaging time.

In the low-pressure system on which experiments are ongoing at Ford, nonexponential time behavior was observed after the decay had progressed to about 0.3 of its original level; this was attributed to ion emission in the photomultiplier. A flame source with OH present at high concentration levels was used as a calibration. It was estimated that within the sampling chamber, 4×10^5 OH could be measured. With a factor-of-2 loss at the sampling orifice, this means detectability of 5 to $8 \times 10^5/cm^3$ at the present time. This could be reduced by a factor of 2 in one hour averaging time; improvements in laser bandwidth and energy should provide another factor of 2 in sensitivity.

Comments

Questions were raised as to the cooling which might occur upon expansion. A Boltzmann plot of the rotational population distribution appeared nonthermal. Are the rotational and translational temperatures the same under these conditions?

ULTRASENSITIVE DETECTION OF ATMOSPHERIC TRACE GASES
USING FREQUENCY MODULATION SPECTROSCOPY

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Frequency modulation (FM) spectroscopy is a new technique that promises to significantly extend the state-of-the-art in point detection of atmospheric trace gases. First introduced in the visible spectral region by Bjorklund (1980), FM spectroscopy is essentially a balanced bridge optical heterodyne approach in which a small optical absorption or dispersion from an atomic or molecular species of interest generates an easily detected radio frequency (rf) signal. This signal can be monitored using standard rf signal processing techniques and is, in principle, limited only by the shot noise generated in the photodetector by the laser source employed. The use of very high ($\sim$ GHz) modulation frequencies which exceed the spectral width of the probed absorption line distinguishes this technique from the well-known derivative spectroscopy which makes use of low (kHz) modulation frequencies.

FM spectroscopy has recently been extended to the 10-μm infrared (IR) spectral region where numerous polyatomic molecules exhibit characteristic vibrational-rotational bands [Cooper and Gallagher, 1985]. In conjunction with tunable semiconductor diode lasers, the quantum-noise-limited sensitivity of the technique should allow for the detection of absorptions as small as 10^{-8} in the IR spectral region. This sensitivity would allow for the detection of H_2O_2 at concentrations as low as 1 pptv with an integration time of 10 seconds. In this workshop we briefly discussed the principles of the technique and the major technical obstacles that must be overcome to achieve quantum-noise-limited sensitivity.

REFERENCES

Bjorklund, G.C., "Frequency-Modulation Spectroscopy: A New Method for Measuring Weak Absorptions and Dispersions," Optics Letters, Vol. 5, p. 15, 1980.

Cooper, D.E., and T.F. Gallagher, "Frequency Modulation Spectroscopy with a CO_2 Laser: Results and Implications for Ultrasensitive Point Monitoring of the Atmosphere," Applied Optics, Vol. 24, p. 710, 1985.

Comments

This method can be applied to both OH, operating in the near ultraviolet with a frequency doubled dye laser, and to HO_2 and H_2O_2 using an infrared laser, such as the diode laser discussed below.

Frequency modulation absorption was seen as a technique which has good future potential as an atmospheric detection method. At the present time, it has been demonstrated at the 10^{-4} level of detectable absorption in laboratory experiments, whereas 10^{-7} will be needed in a field instrument in order to be generally useful for atmospheric monitoring. The obstacles to future development comprise a long list of technical issues, which are likely to be solved with further improvements in laser and modulation devices.

Thus, the workshop participants generally agreed that FM spectroscopy was not currently ready for full-scale intrument development, in order to make field measurements of OH in a few-year time scale. Concern was expressed as to whether it would ever be capable of measuring OH in the near future. However, its general applicability to a wide variety of atmospheric species makes it a very attractive and logical extention of absorption methods. Well-designed experiments examining the best spectral regions for study along with a systematic investigation of pressure effects (line broadening) should be considered for funding. Collaboration between researchers experienced in atmospheric absorption spectroscopy and those knowledgeable about FM methods should be encouraged. Steps should be taken toward laboratory measurements on typical air samples.

REMOTE DETECTION OF OH

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The details of the proposed JPL experiment to monitor [OH] are reasonably well summarized in the proceedings of the previous, 1982 H_xO_y Workshop (NASA Conference Publication 2332, p. 25, 1984).

This is a remote measurement technique utilizing a XeCl excimer laser tuned to the Q_211 rotational transition of the $0-0$, A−X band at 307.847 nm. A wavemeter is under development to monitor, on a pulse−to−pulse basis, both the laser lineshape and absolute wavelength (this should be operational by fall '85). Fluorescence is detected with a multiple Fabry−Perot type filter with a spectral resolution on the order of 0.001 nm. This is tuned to the overlapping Q_22, Q_122, Q_23 and Q_123 rotational transitions at 308.986 nm. The fringe pattern from this filter is imaged using a discrete, multi−anode detector which has a photon gain of 10^8. This permits the simultaneous monitoring of OH fluorescence, N_2 and/or O_2 rotational Raman scattering and broadband background levels. The use of three etalons in series provides sufficient rejection, $\geq 10^{10}$, against the laser radiation only 1.2 nm away.

Advantages of 308 nm excitation:

    higher absorption cross section
    less ozone absorption
    less artificial OH generation
    simpler relaxation kinetics
    efficient, high power, tunable transmitter available

Advantages of FP multispectral detector

    simultaneous measurement of fluorescence, background and normalization
        intensities − requires only one laser and one wavelength
    greatly reduced solar, and other broadband, background

In summary, the 308 nm scheme would yield an increased fluorescence signal and a reduction in the level of interference, by many orders of magnitude compared to the measurements reported to date. The technique provides a realistic sensitivity at the $[OH] = 10^5$ molecule cm^{-3} level.

Comments

The 308-nm excitation scheme presented by the JPL researchers seemed reasonably possible of achieving the required sensitivity. However, the triple etalon, with a 10^{14} contrast ratio at a bandpass of 0.001 nm, seemed very risky to most of the workshop participants. Measurements on and off line can be used in conjunction with rotational Raman to yield multiple species measurements. The projected high sensitivity with short integration times suggests a more detailed examination of the scheme would be valuable, although satisfactory manufacture of the etalon seemed itself to be a major technological achievement. Concern was expressed over off-axis solar radiation and the level of interference it would cause.

In order to reduce lidar data to absolute concentrations, independently determined collisional cross sections are needed. For this narrowband work, this includes rotational transfer and quenching on a state-specific basis. This contrasts with the sampling systems where calibrations can be used. However, it was felt that high accuracy was here not an important issue; high-precision measurements were of value and ultimately the accuracy could be determined. A pooling of the knowledge of those people experienced with such etalons should be brought together in an experiment demonstrating the high rejection of both on-axis and off-axis light.

INDIRECT DETERMINATION OF OH

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Integrated global OH estimations have been made in the past from an analysis of the emissions and atmospheric budgets and distributions of a variety of man-made halogenated species (methyl chloroform, dichloromethane, 1,2 dichloroethane and tetrachloroethylene) which are believed to be exclusively removed by reaction with OH and are considered to have no significant natural sources. Because of source complexities somewhat less precise estimations of OH have also be made by employing naturally occurring species such as ^{12}CO and ^{14}CO. These techniques to date suggest that the seasonally averaged global OH abundance is about 5 x 10^5 molec/cm^3.

More recently efforts are under way to develop indirect OH measurement techniques by utilizing tailor made "reactive OH tracers" to be employed in estimating OH abundance within air masses over a 10^2-10^3km transport distance. By simultaneously releasing controlled quantities of reactive and inert tracers, both dispersion and OH abundance can be determined. When fully developed, the method will be useful at all expected levels of atmospheric OH concentrations (<10^5-10^8 molec/cm^3). A number of candidate "reactive OH tracers" have been selected after a careful screening process. Laboratory work is now under way to affirm the applicability of the selected chemicals to real world conditions.

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[*]work performed at SRI-International, Menlo Park, CA 94025.

Comments

From considerations of ways to measure OH in the polluted Los Angeles environment using chemical releases, there are several hydrocarbons which by ratio measurements can achieve sensitivities of 2 to 3×10^6. Toluene/benzene and ethyl benzene/benzene ratios can furnish 1×10^6. Other candidates are fluorinated hydrocarbons specially manufactured for the purpose.

Questions were raised as to the photochemistry of the species chosen, and whether they would perturb the local chemistry controlling OH. An inert tracer should always be released along with the reactive species. The mixing time should also be known well; if it is too close to the reaction time, that species is a poor choice unless an inert tracer accompanies it. The photochemical models should be used to design the release experiments.

MEASUREMENT OF ATMOSPHERIC HO BY A CHEMICAL METHOD

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University of California
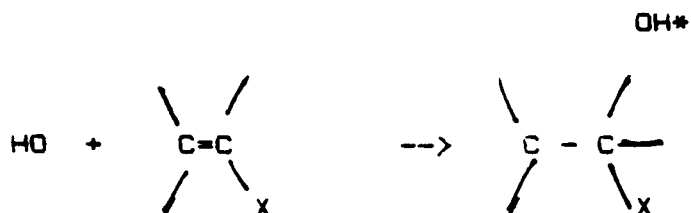Irvine, California

The development of a sensitive chemical technique for the measurement of atmospheric hydroxyl radical concentrations is highly desirable in view of the lack of significant success with current spectroscopic methods. The parameters for a chemical technique can be outlined from the following set of desirable goals: (1) sufficient conversion of tracer species A to product B that B can be measured quantitatively in the presence of A and a great excess of air; (2) specificity of reaction such that A is converted to B only by reaction with HO; and (3) sufficient sensitivity for detection that the ambient concentration of HO is not seriously perturbed by the presence of A and B. The chemical method previously attempted has involved the use of ^{14}CO as a tracer and radiochemical measurement of the $^{14}CO_2$ formed by its oxidation by atmospheric HO.[1] The rate constant for this reaction at 298 K and one atmosphere pressure is about 10^{-13} cm^3 molecule^{-1} sec^{-1}. With HO concentrations in the range 10^4 to 10^7 cm^{-3}, this rate constant is too small to allow formation of sufficient quantities of the $^{14}CO_2$ product in a time period short enough to avoid containment problems for the air mass under test (conversion of 10^{-7} to 10^{-4} per second). This technique was not ready for field application and failed in the NASA-CITE comparison test.

The problems encountered with the HO + ^{14}CO system can be minimized if a reaction of HO forming a specific product can be found with a rate constant up to 100 times faster than with CO. The HO concentration in

remote atmospheres is believed to be controlled chiefly by reaction with

CO, whose concentration lies in the 50-150 ppbv range. The limitation

on concentration of tracer A is actually an upper limit on total

reactivity with removal of HO by reaction with A no more than 10% as

large as removal by reaction with CO. With this 10% upper limit on

total reactivity as a criterion, a 100-fold increase in HO reactivity of

A relative to CO would limit the concentration of A to 10^{-3} x [CO], i.e.

to 50-150 pptv. If the tracer species A reacted with HO only 10 times

as rapidly as with CO, then the atmospheric concentration limitation

would be relaxed to 10^{-2} x [CO] for the tracer reactivity criterion.

In addition to a rapid rate constant with HO and specificity of the

reaction product, a useful monitor reaction must also satisfy other

requirements, such as (a) the background levels of A and B in the

atmosphere should be negligible; (b) other removal processes in the

atmosphere should be negligible for both the A and B; and (c) A and B

must be separable from the air mass and from one another for

quantitative assay.

The addition reactions of HO with various alkenes and alkynes are

known to occur with rate constants in the range of 10^{-12} to 10^{-11} cm^3

molecule^{-1} sec^{-1},[2] forming a vibrationally excited adduct radical:

$$
\begin{array}{ccc}
 & & \text{OH*} \\
\text{HO} + \quad \overset{\displaystyle \diagdown \quad \diagup}{\underset{\displaystyle \diagup \quad \diagdown_X}{C=C}} & \longrightarrow & \overset{\displaystyle \diagdown \quad \diagup}{\underset{\displaystyle \diagup \quad \diagdown_X}{C - C}}
\end{array}
$$

Such excited radicals usually can then undergo either collisional

stabilization or unimolecular decomposition. With olefins containing

weakly bonded substituents, the possibility exists that a fast decomposition channel for the adduct radical could be found leading to a specific product (e.g. loss of X in the example above.)

The substituents R can be constructed to have electronegative components such as chlorine atoms which will facilitate highly sensitive product measurement by gas chromatography-electron capture techniques. The use of symmetric substituent molecules such as X-C=C-X might be

$$X-\underset{R}{\overset{|}{C}}=\underset{R}{\overset{|}{C}}-X$$

expected to enhance the product yield. Analogous reactions are known to occur with atomic fluorine or chlorine atoms and various haloalkenes, as in F + CH$_2$=CHBr --> CH$_2$=CHF + Br, and F + CH$_2$=CH-CH$_2$Cl --> CH$_2$F-CH=CH$_2$ + Cl. In the latter case, the decomposition of an adduct radical by loss of the Cl atom occurs so rapidly that more than 99% of these radicals decompose at one atmosphere pressure to give the CH$_2$FCH=CH$_2$ product.[3] It is quite possible that similar reaction channels can be found following HO attack on suitably substituted olefins. Laboratory measurements of product yields and rate constants for their formation are required to determine whether a reactant molecule can be found which has the necessary properties for determination of local HO radical concentrations.

(1) M. J. Campbell, J. C. Sheppard and B. B. Au, Geophys. Res. Lett., 6, 175 (1979).

(2) R. Atkinson, K. R. Darnall, A. C. Lloyd, A. M. Winer and J. N. Pitts, Jr., Advances Photochem., 11, 375 (1979).

(3) R. S. Iyer, L. Vasi and F. S. Rowland, J. Phys. Chem., in press.

Comments

This proposed study involves finding a chemical reaction specific enough for OH, and a measurement of the product formed. What one wants is a rate constant of about 10^{-10} cm^3 s^{-1}, so that 0.1 percent of the OH will be converted in 100 s. Laboratory studies are needed to find a reaction which will fill this bill, yielding a product in quantity sufficient for precise measurement. This is an extremely fast rate constant and the search may be difficult. Again there is a question of perturbing the local environment, while still providing a sensitive measurement. Also the temperature and pressure dependence of the reaction rate is a complicated function for many of these species (that is, one must use an RRKM or Troe-based picture), and must be taken into account.

THE DETERMINATION OF THE GLOBAL AVERAGE OH CONCENTRATION
USING A DEUTEROETHANE TRACER

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Ralph Cicerone
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It is proposed to measure the decreasing global concentration of an OH reactive isotopic tracer, C_2D_6, after its introduction into the troposphere in a manner to facilitate uniform global mixing. Analyses at the level of 2×10^{-19} mole fraction, corresponding to one kg uniformly distributed globally, should be possible by a combination of cryogenic absorption techniques to separate ethane from air and high sensitivity isotopic analysis of ethane by mass spectrometry.

Aliquots of C_2D_6 totaling one kg would be introduced at numerous southern and northern latitudes over a 10 day period in order to achieve a uniform global concentration within 3 to 6 months by the normal atmospheric circulation. Then samples of air of 1000 ℓ (STP) would be collected periodically at a tropical and temperate zone location in each hemisphere and spiked with a known amount of another isotopic species of ethane, $^{13}C_2H_6$, at the level of 10^{-11} mole fraction. After separation of the ethanes from air, the absolute concentration of C_2D_6 ($C_2D_6/^{13}C_2H_6 \sim 10^{-8}$) would be analyzed using the Argonne 100-inch radius mass spectrometer. The effective global average concentration of OH is determined by

$$\overline{[OH]} = \frac{1}{kt} \log \frac{[C_2D_6]_o}{[C_2D_6]_t}$$

where the rate constant for the oxidation of C_2D_6 by OH, $k = 3.06 \times 10^{-11} \ell \, \text{cm}^3 \, \text{molecule}^{-1} \, \text{sec}^{-1}$ (C. M. Stevens and Bunschul, unpublished). For an average OH concentration of 10^6 molecules/cm^3 the lifetime is 1.1 years.

Concentration differences of C_2D_6 due to hemispheric and seasonal differences in OH concentration should be observable within the expected accuracy of the analyses of $\pm$ 1 to 3%.

The principal technical difficulties are expected to be non-uniformities in the mixing of the tracer and the uncertainty of the competitive scavenging of C_2D_6 by Cl radicals (Chiltz et al., 1963), estimated at 20% of the OH removal rate (Aiken et al., 1982).

Chiltz, G., R. Eckling, P. Goldfinger, G. Huybrechts, H. S. Johnson, L. Meyers, and G. Verbeke, J. Chem. Phys. 38, 1053 (1963).
Aiken, H. C., J. R. Herman, E. J. Maier, and C. J. McQuillan, "Atmospheric Chemistry of Ethane and Ethylene," J. Geophys. Res. 87, 3105-3118 (1982).

Comments

This concept received widespread approval from many workshop participants, not as a check on current levels of OH but as a method to set a series of measurements to be carried out over many years. The idea is to repeat the measurements over each 5 to 10 year period for several decades. It can then be used to obtain a determination of any change in the oxidizing capacity of the atmosphere, a parameter of direct utility in forecasting future changes (one estimate places a 25 percent decrease in this quantity over the last 35 years). For example, has the increase in tropospheric ozone increased or decreased OH?

With a large mass spectrometer as suggested here, 10^{-10} mole fraction of the released reactant can be determined in 5 minutes. A fully globally mixed 1 kg sample will yield 6 molecules/cm^3. The choice of C_2D_6 is a good one but should be looked at further. Are there any possibilities that it will be released outside this experiment, thus contaminating the results? (What are other uses for this compound?) Background measurements should be made to address this; these should be easy to do. There is concern about the effects of $C\ell$ atoms in the atmosphere; at likely concentrations worldwide and with probable reaction rates, they will account for about 20 percent of the total C_2D_6 loss rate according to some estimates. Another participant however felt there was too little $C\ell$ in the troposphere to cause any loss.

Perhaps less ambiguity can be achieved using other compounds, for example $CD_3CF_2CD_3$, which is less common and will have far less contamination. Of course, reaction rates will need to be carefully determined in the laboratory. Multiple releases using different reactants (the use of three was suggested) may be valuable in this regard. Unsaturated compounds react with O_3 not OH, so saturated hydrocarbons are better.

Of major concern are large nonuniformities in concentration resulting from release and subsequent circulation patterns. These could cause a large error in the decay rate if not properly accounted for including nonuniformities in the oxidizer concentrations. Calculations with a global circulation model are needed here. For example, the concentration of C_2H_6 has been found to vary at certain locations by a factor of 3 on a seasonal basis. Nonreactive tracers would help here although no suitable species has been found for this purpose yet. Some participants were concerned about errors in the measurements, that is, nonrepeatability due to differences in tropospheric circulation and chemistry. This was estimated as high as 15 percent for a given measurement for a homogeneously released compound with a chemical lifetime of one year, measured one year after release. For the C_2D_6 considered here, things could be worse. Again, calculations with a global circulation model need to be performed to address these questions.
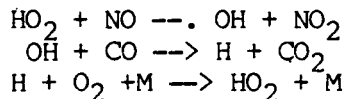
PEROXY RADICAL DETECTION BY CHEMICAL AMPLIFICATION (PERCA)

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Important reactions of atmospheric free radicals are the chain oxidation of NO and CO. Thus:

$$HO_2 + NO \longrightarrow OH + NO_2$$
$$OH + CO \longrightarrow H + CO_2$$
$$H + O_2 + M \longrightarrow HO_2 + M$$

In most models, the need to know the free radical concentration could also be described as the need to know the rate of the above oxidation chain in the atmosphere. It is the total rate of this chain (also carried by RO_2 and RO) which we measure using the PERCA. The PERCA is thus essentially a RO_x meter (with apologies to our geological colleagues). The PERCA works by adding excess CO (10%) and NO (5ppm) to a stream of air and measuring the NO_2 produced after 3s of reaction time. Since other processes produce NO_2, the chain reaction is modulated by switching the CO for N_2. The chain length is limited by the reaction OH + NO $\longrightarrow$ HONO and is modeled to be somewhat over 1000. Measured chain lengths agree with the modeled numbers.

The instrument as presently configured weighs 35 lbs. and draws 1 amp. of 110v power. It uses cylinders of pure CO and 100 ppm NO in N_2. Measurements in the laboratory and in air at ground level have been made. In the laboratory sensitivity has been demonstrated to concentrations of total HO_x free radicals believed to be of order 10^{-3} pptr ($\sim 2.5 \times 10^4$ cm^{-3}). In the field, the high variable NO_2 background from NO_2 and O_3 + NO $\longrightarrow NO_2$ has limited sensitivity to 10^8 cm^{-3}.

All RO_2 radicals which react fast with NO to produce NO_2 are expected to be measured with equal sensitivity. Atmospheric PAN and HNO_4 are not an interference unless they decompose during the 3s reaction time. The effect of that interference has been modeled, but not yet measured. Fortunately, it is self-limiting. At high temperatures decomposition is faster in the cell, but, for the same reason, under most circumstances, at higher temperatures, there is expected to be less PAN and HNO_4 in the atmosphere.

Bibliography:

"Measurement of Atmospheric Peroxy Radicals by Chemical Amplification", C.A. Cantrell, D.H. Stedman, and G.J. Wendel, Analyt. Chem. 56, 1496, 1984.

"A Possible Technique for the Measurement of Atmospheric Peroxy Radicals", C.A. Cantrell and D.H. Stedman. Geophys. Res. Lett. 9, 846, 1982.

"Laboratory Studies of an HO_2/RO_2 Detector", D.H. Stedman and C.A. Cantrell. Proceedings of the AMS Conference on Non-Urban Troposphere, Williamsburg, VA., May, 1982.

Comments

The concern by the workshop participants about this method was directed to its lack of specificity and, under some conditions, the stability of the chemical amplification employed.

FLUOROMETRIC METHOD FOR THE DETERMINATION OF GAS-PHASE HYDROGEN PEROXIDE

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The fluorometric gas-phase hydrogen peroxide procedure is based on the technique used by Lazrus et. al. (1) for the determination of H_2O_2 in the liquid phase. The analytical method utilizes the reaction of H_2O_2 with horseradish peroxidase and p-hydroxphenylacetic acid (POPHA) to form the fluorescent dimer of POPHA. The analytical reaction responds stoichiometrically to both H_2O_2 and some organic hydroperoxides. To discriminate H_2O_2 from organic hydroperoxides, catalase is used to preferentially destroy H_2O_2. Using a dual-channel flow system the H_2O_2 concentration is determined by difference.

For the determination of H_2O_2 in the gas-phase, the liquid-phase analytical procedure is used with an inlet system which concentrates H_2O_2 in the aqueous phase. The following figure details the inlet system.
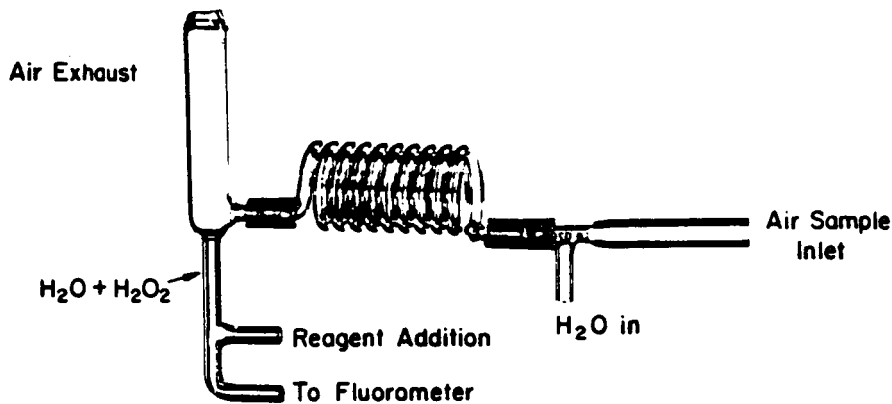
Sample air at 2 slpm along with .042 ml/min of aqueous solution is drawn through the scrubbing coil. The H_2O_2 is extracted into solution and analyzed directly using the fluorometric procedure. The detection limit for gas-phase H_2O_2 is better than 50 pptv. The system has been tested for potentially interferring species commonly found in the atmosphere. Minor interferences from sulfur dioxide (SO_2) and ozone (O_3) are observed. Sulfur dioxide gives an interference at a level of 1% of the H_2O_2 signal for each 10 ppbv of SO_2. The O_3 interference generates a H_2O_2 signal equivalent of 30 pptv for each 100 ppbv of O_3.

The gas-phase analytical system has been used on a number of ground and aircraft based field studies in the past year. Measured levels of H_2O_2 range from the detection limit to several ppbv.

[1]A. L. Lazrus, G. L. Kok, S. N. Gitlin, J. A. Lind, and S. E. McLaren, Analytical Chemistry 57, 917 (1985).

Comments

This instrument has received much flight time and appears capable of detection limits < 50 ppt with minimal interference (chief culprits are SO_2 and O_3). Future improvements include the inlet system, the response time, and the ability to separate H_2O_2 from RO_2H. A calibration between this instrument and the tunable-diode laser determination has been performed at the 3-5 ppb level, which was near the detection limit for the diode system. It was reported at the workshop that satisfactory agreement between the two instruments was observed. This is important in that the spectroscopic method is very specific for H_2O_2 but not as sensitive as the fluorometric method.
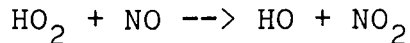
TROPOSPHERIC HO$_2$ DETERMINATION BY FAGE

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Portland, OR

In contained-flow HO analyzers, ambient HO$_2$ can be detected by its conversion to HO via

$$HO_2 + NO \longrightarrow HO + NO_2$$

The detection efficiency is greatest at low pressures, where the subsequent removal of the HO product by the NO reagent (via HO + NO + M $\longrightarrow$ HONO + M) is relatively slow. Moreover, nozzle expansion of the air from ambient to low pressures produces a turbulent zone that assists in mixing the reagent with the sample. If the HO product is observed by laser-excited fluorescence, then the other advantages of low-pressure detection by FAGE (Fluorescence Assay with Gas Expansion) also apply.

The method and some of its potential interferences are set forth in Reference 1. Regarding RO$_2$, we incorrectly assumed that the intermediate reaction RO + O$_2$ $\overset{\text{\tiny 2}}{\longrightarrow}$ R'CHO + HO$_2$ is instantaneous in our pressure range; correction reduces this interference considerably. When NO is the modulating reagent, any contaminant that fluoresced (or gave photolytic HO) would produce a false positive HO$_2$ signal. This can be prevented by using a steady NO flow, modulating the resulting ambient HO$_2$ + HO signal with an HO-removing reagent, and performing a parallel determination of ambient HO in another channel.

We have calibrated the FAGE instrumental response to external HO$_2$ by observing NO decay in the photolysis of HO-CH$_2$O mixtures and by choosing conditions in which HO$_2$ + NO is the only significant NO destruction path. We have determined HO$_2$ in urban air.

Reference

T.M. Hard, R.J. O'Brien, C.Y. Chan and A.A. Mehrabzadeh, Environmental Science and Technology <u>18</u> 768-777 (1984).

Comments

Using this chemical conversion/LIF detection of OH method, this group estimates that HO_2 can be detected at levels of 60 to 120 × 10^6/cm^3 in a 6-minute average. They claim it is specific to HO_2 in that other peroxyl radicals, such as methyl peroxyl, can be prevented from yielding OH at low pressure due to kinetic freezing out. Current calibrations are by NO decay due to HO_2 + NO in the absence of O_3, and HO_2 decay due to HO_2 + NO_2 in the absence of NO, NO_2, and O_3. These two methods give differing results by a factor of 2, and it will be necessary to resolve such discrepancies. The workshop participants felt that the method appeared sound from a spectroscopic/laser basis, but that there remained questions concerning its chemical aspects.

TUNABLE-DIODE LASER ABSORPTION SPECTROMETRY

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Tunable-diode laser absorption spectrometry (TDLAS) affords a number of advantages for atmospheric measurements. It is a universal method, applicable, in principle, to all gases of atmospheric interest. Because of its extremely high spectral resolution it provides unequivocal identification of the target species, with no interferences from other gases. It provides real-time, in situ measurements with time resolutions better than 1 minute.

We have constructed TDLAS systems suitable for both ground-based and airborne measurements. Although great improvements have been made in the detection limits achievable by these systems they are currently incapable of measuring HO at atmospheric concentrations. However, the addition of the new megahertz modulation techniques (proposed by D. E. Cooper) may make HO measurements attainable by TDLAS.

The sensitivity of the current TDLAS system is marginally capable of measuring HO_2. This species exists in the troposphere at concentrations which are up to 2 orders of magnitude higher than those of HO and, in addition, is much less susceptible to removal by the surfaces of the instrument and its sampling system. HO_2 is an important HO_x species in its own right but can also give direct information on the HO concentration by virtue of the rapid partitioning between these two species. The addition of the high-frequency modulation technique to the TDLAS system would ensure its ability to measure HO_2 under most atmospheric conditions.

On the other hand, we have demonstrated (Slemr et al., J.G.R.), the ability of the TDLAS to measure hydrogen peroxide (H_2O_2) in the ambient atmosphere. With the airborne system the detection limits should be better than 0.1 ppbv, which is sufficient to measure this species under most atmospheric conditions. H_2O_2 measurements give a clear indication of HO_x mixing ratios and are also important as a photolytic source of HO and as an important oxidant for other atmospheric consitituents such as SO_2.

Reference

Slemr, F., Harris, G. W., Hastie, D. R., MacKay, G. I., and H. I. Schiff.
   J. Geophys. Res., vol. 9, no. D5, pp. 5371-5378, April 1986.

Comments

This instrument can be used for both NO_2 and H_2O_2, with current limits of detectability at 40 and 300 ppt, respectively. This is acheived in 1 to 10 minutes of averaging, using a 0.7-m path length multipassed for a total absorption path of 40 m, allowing absorption at the 10^{-5} level to be measured. Improvements in the multipass capability should increase the path length to 200 m, lowering the detection limits to below 20 and 100 ppt for these two species.

Detection of HO_2 is marginal at the 10^8 per cm^3 level, but a combination with frequency modulation spectroscopy, such as discussed at the workshop by D. E. Cooper of SRI, may make this a viable method.

Standard Bibliographic Page

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16. Abstract

This report documents the activities and recommendations of the NASA workshop on the Future Directions for H_xO_y Detection which was held in Menlo Park, California, August 12 through 15, 1985. The workshop was sponsored by NASA's Tropospheric Chemistry Program as part of a continuing effort to direct its applications programs toward national needs.

The objective of this workshop was to assess future directions for the measurement of the OH radical as well as other H_xO_y species. The workshop discussions were focused by two broad questions: (1) What are the capabilities of potential measurement methods? and (2) Will the results from the most promising method be useful in furthering understanding of tropospheric chemistry?

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