Confidence Is Growing in Tropospheric OH Measurements

There aren't many hydroxyl molecules (OH) in the troposphere, but the few that are there certainly make their presence known. More than any other species in the troposphere (the atmospheric layer between Earth's surface and an altitude of 8–18 km), the OH radical determines the lifetimes of such common atmospheric constituents as carbon monoxide, methane and sulfur dioxide. Yet, because of its short atmospheric lifetime (a single molecule sticks around less than one second) and low concentrations (a few tenths of a part per trillion, compared, for example to carbon dioxide levels, which are a few hundred parts per million), the OH radical has defied accurate measurement. Not any more.

In the past five years, researchers have increased the sensitivity of several types of instruments to permit precise readings of OH concentrations. These instruments are now being sent on major field studies of atmospheric photochemistry. Some of the most sensitive instruments, however, rely on indirect calibrations. That's why researchers have welcomed a series of increasingly successful comparisons of OH measurements made at the same time and the same place by different techniques. The most recent of these comparisons, reported in *Geophysical Research Letters* in September by a group at the Institute for Atmospheric Chemistry at the Jülich Research Center (KFA) in Germany involved purely local measurements.[1-3]

The role of OH

The important role that the OH radical plays in the atmosphere started to become clear in 1971, when it was hypothesized[4] that OH is formed in the atmosphere when sunlight breaks down ozone molecules; a few of the metastable oxygen atoms thus produced react with a water molecule to give OH. OH can react quickly with CO to yield CO_2, and with methane and other hydrocarbons to form formaldehyde. In the process, OH is converted to HO_2 (hydroperoxyl), from which OH can be regenerated to start the chain all over again.

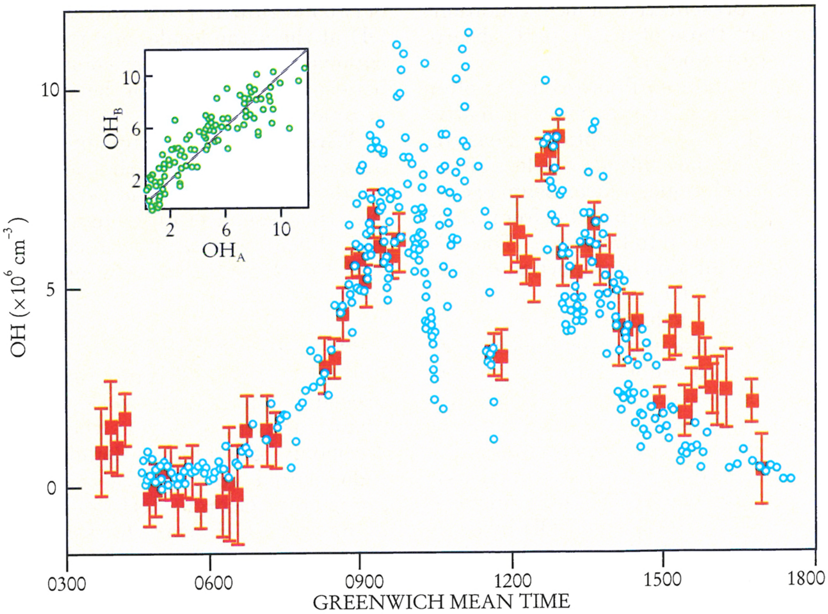
After spending many frustrating years trying to develop instruments sensitive enough to sniff out the elusive hydroxyl radical in the troposphere, researchers are finally able to send different types of instruments on field studies and to get similar readings from them.

Once the importance of OH was known, the race was on to build an instrument to detect it.[5] A number of problems plagued the efforts, and comparisons between OH instruments in 1983–84 yielded discouraging results. As lessons were learned, both new and improved instruments emerged. In 1991 and 1993, two more comparisons were made in the mountains of Colorado, and this time the outcomes were favorable: Researchers started to gain confidence that the instruments were all measuring the same thing.

Both of the Colorado-based comparisons involved an absorption instrument whose reading gave an average over a roughly 10 km horizontal path, along which the OH concentration can vary. Since then, there have been two comparisons between colocated *in situ* instruments—that is, ones that measure OH at essentially a point location. The 1994 Jülich experiment was one of the local comparisons.

Ways to measure OH

Two of the instruments developed to measure OH levels are laser-based devices: a differential optical absorption



CONCENTRATIONS OF THE HYDROXYL RADICAL as measured by a group from the Jülich Research Center (KFA) in Germany using colocated spectrometers, one based on laser absorption (red squares) and the other on laser-induced fluorescence (blue circles). During clear skies in the early morning (before 0900 Greenwich mean time), data points track well, but fluctuate under variable clouds in the afternoon. After 1500 the absorption instrument gives higher readings, as was the case whenever the winds blew from the northwest. Discarding such data, the Jülich researchers get the correlation seen in the inset, where labels OH_A and OH_B refer to data taken with the fluorescence and absorption instruments, respectively. (Adapted from ref. 3.)

spectrometer, which has a reliable calibration, and a laser-induced fluorescence spectrometer which is more portable and senses the OH levels at a specific location; the fluorescence spectrometer has been proven to be quite sensitive.

A differential optical absorption spectrometer measures the absorption of laser light by OH molecules as the beam travels through the atmosphere from a transmitter to a distant mirror and back again. Calculating the OH concentration from the observed dips in absorption depends only on well-known spectroscopic parameters, so that the calibration is intrinsically accurate. However, to get measurable amounts of absorption, one has to make the laser path length very long—on the order of kilometers. The concentrations of the OH radical frequently vary along this path, so that this method determines an average value.

The distance from transmitter to mirror in the absorption spectrometer doesn't have to be so long: It can be folded by setting mirrors much closer together and reflecting the light back and forth to give the desired path length. For example, the Jülich group developed a folded-path interferometer in which the mirrors are separated by less than 40 m but the effective path length is several kilometers. The readings of a folded-path instrument are more representative of local conditions than are those of a long-path absorption spectrometer.

Laser-induced fluorescence is often considered to be a more sensitive method than absorption measurements, but the calibration is less direct. In this technique, a laser beam excites the OH molecules to states from which they are known to fluoresce. The subsequent radiation is proportional to the number of OH molecules in the air sample. To deduce the concentration of OH from the measured fluorescence, one needs to calibrate the instrument with a known quantity of OH fed from an external source. That's where the uncertainty in calibration enters.

The earliest ground-based versions of the fluorescence instrument inadvertently generated spurious OH by dissociating atmospheric ozone, but those problems have now been averted by operating the laser at a lower pressure.[6]

Several other instruments have been developed that do not rely on a laser. Fred Eisele and his colleagues from Georgia Tech and the National Center for Atmospheric Research (NCAR) have built an ion-assisted OH detector that identifies OH based on its reaction with sulfur dioxide to form sulfuric acid. A group at Washington State University uses a method based on the oxidation by OH of a known quantity of radioactive ^{14}CO, and a second group there uses a gas-to-liquid scrubbing technique.

In situ comparison

For their 1994 comparison, the Jülich experimenters compared the readings of their folded-path absorption spectrometer to those of a laser-induced fluorescence spectrometer. They took the instruments to an agricultural field in the German countryside to study the photochemistry of plant-emitted compounds and OH radicals. Typical results from one day are shown in the figure on page 17. Measurements from both instruments show the rise of OH concentrations in the middle of the day and the decline at night. In the clear sky that prevailed before 0900 Greenwich mean time, the data points fell on top of one another, but between about 0900 and 1500, a variable cloud cover caused the OH levels to fluctuate. The two sets of measurements disagreed with each other most sharply after about 1500, when the winds were blowing from the northwest. The researchers speculate that the northwest winds must have been blowing in precursors of OH from some local source near the absorption instrument.

David Crosley of SRI International in Menlo Park, California is concerned about the variation with wind direction of two instruments that are measuring OH at the same locale, and the implications it might have for comparisons between instruments or between instruments and models.

When the Jülich group omitted the data corresponding to the northwest winds and plotted one data set against the other (see inset in the figure), they got a linear regression with a slope of 1.01 ± 0.04 and a correlation coefficient r of 0.9.

Colorado comparisons

In the 1991 and 1993 comparisons that preceded the Jülich work, George Mount and his group at the NOAA Aeronomy Laboratory in Boulder, Colorado, paired up with Eisele and his group from Georgia Tech and NCAR to measure OH near the same site. Mount used a differential optical absorption spectrometer whose path stretched from Fritz Peak in Colorado to the Caribou mine about 10 km away (and just slightly higher in elevation). Eisele's group set up the ion-assisted OH measurement instrument, which measures OH locally, at the Caribou site. This 1991 comparison was a milestone because it established credible correlation between two OH instruments.[7]

In 1993 the Georgia Tech–NCAR–NOAA teams not only improved but expanded the scope of the OH comparison campaign to include measurements of a host of other tropospheric constituents that affect OH concentrations, so that the measured OH could be compared to that predicted by photochemical computer models. They were joined in the venture by additional NCAR colleagues, as well as by researchers from Pennsylvania State and Washington State Universities and from the University of Minnesota. The participants will publish 26 papers reporting their measurements in a special issue of the *Journal of Geophysical Research* early next year.[8]

The experiment involved the determination of OH levels by four different techniques, but only two of them—the ion-assisted measurement and the long-path optical absorption technique—generated sufficient data to permit a significant comparison. To minimize the effect of variable OH levels along the 10 km path, the researchers focused their comparisons on times when the OH levels were uniform (as inferred from meteorological data and from measurements of several other photochemical compounds along the same path). Then, the data from the two detectors agreed within the standard error of 15% nearly all the time. The OH levels measured by the absorption instrument were on average about 20% higher than those determined by chemical means. Mount told us that his group is working to understand the discrepancy.

One major result of the 1993 campaign was that, in clean air, the OH levels predicted by the models are about 50% higher than those measured in the field. (The agreement is better in dirty air.) As predicted in 1981, the OH concentrations rose and fell in step with the levels of NO_x, and they showed the expected relation to the water and ozone molecules involved in OH production.

Measurement campaigns

Armed with new confidence, the researchers have been taking their OH instruments on a number of field experiments. We caught up with Eisele freshly returned from having flown his instrument aboard an aircraft as part of NASA's Pacific Exploratory Mission in the Tropics. Eisele's group has also measured OH both on the ground and in the air on two other field studies. William Brune of Penn State recently took a fluorescence spectrometer aboard an aircraft as part of a mission called SUCCESS, to study clouds and aircraft contrails. Thomas Hard of Portland State University has been measuring OH to study pollution in Los Angeles. Paul Wennberg, working with James Anderson at Harvard University, has been looking at the OH levels in the upper troposphere using a fluorescence-based instrument originally built for stratospheric measurements; they have provided some of the first measurements of OH in the upper troposphere. And the Jülich group has now set sail southward on the Atlantic Ocean from Bremerhaven, measuring OH concentrations with both the absorption and fluorescence spectrometers.

Field experience with the OH instruments—and the improvements it will motivate—will add to their credibility, but no one will have full confidence in them until independent parties conduct a blind comparison.

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Precision Tests Find No Violation of Bose Statistics

Very stable tunable lasers now make it possible to test Bose statistics to a part in a million. The oxygen nucleus has passed the test.

The symmetrization postulate of quantum mechanics asserts that the multiparticle wavefunction for any collection of identical particles must be either wholly symmetric or wholly antisymmetric under the exchange of labels between any two particles. In nonrelativistic quantum mechanics, this postulate is a somewhat *ad hoc* assumption tacked onto the theory; wholly symmetric or antisymmetric wavefunctions are not the only ways of preserving the indistinguishability of identical particles.

But even in the relativistic theory, where Lorentz invariance and the existence of antiparticles seem to force the spin–statistics theorem on us, there might be room—though not without cost—for small violations of strict Bose or Fermi statistics. A phenomenological theory of small violations of the symmetrization postulate, proposed in 1991 by O. W. Greenberg at the University of Maryland,[1] provides a parametrization for experimenters testing the limits of conventional identical-particle statistics.

The Pauli exclusion principle makes it possible for experimenters to test the Fermi–Dirac statistics of electrons with awesome precision. By looking for x rays from injected electrons falling into already occupied inner orbitals in a strip of copper, Eric Ramberg and George Snow at Maryland were able to show in 1990 that, at most, one or two electrons in 10^{26} dared violate the exclusion principle.

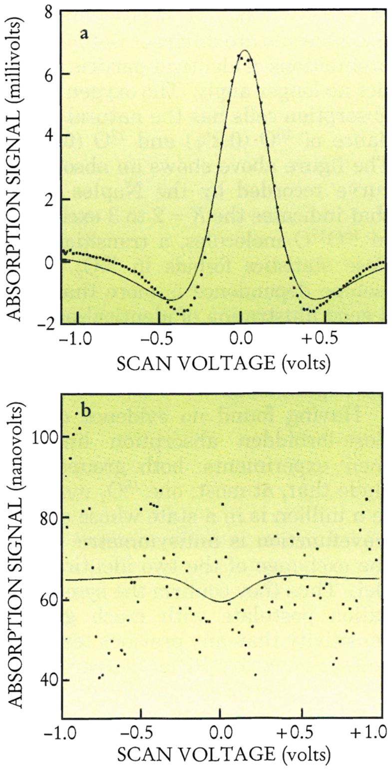
Bose–Einstein statistics, however, don't offer the experimenter anything quite as convenient as the exclusion principle. Only now, with the appearance of two papers, back to back, in a recent issue of *Physical Review Letters*, do we have the first high-precision tests of identical-particle statistics for bosons.[2,3] Exploiting the extremely stable tunable diode lasers that have been available only in the last few years, groups at the University of Naples[2] and Amherst College[3] have shown that if there is any violation of Bose statistics by the identical spin-0 oxygen nuclei in $^{16}O_2$ molecules, it does not exceed a part in a million.

It has been known since the 1920s that the suppression or absence of half the usual complement of spectral lines in the rotation spectra of diatomic molecules with identical nuclei could be attributed to Bose or Fermi statistics, depending upon whether the nuclear spin is integral or half-integral. In the case of $^{16}O_2$, Bose statistics permits only molecular rotation states of odd rotation quantum number K in the electronic ground state, whose wavefunction, apart from rotation, is antisymmetric under exchange of the nuclei. Conversely, excited $^{16}O_2$ states with symmetric electronic wavefunctions are required by Bose statistics to have K even. But traditional optical spectroscopy had only verified that the Bose-forbidden states were suppressed by a factor of 10^{-2} or 10^{-3} relative to the Bose-allowed states.

That left lots of room for the small, surreptitious violations of Bose statistics that theorists have lately been toying with. If, for example, one conjectured[4] that the anomalous decay of long-lived neutral K mesons into pion pairs was due entirely to violation of Bose statistics (rather than CP violation), one would need a violation only on the order of 10^{-6}.

Testing with spin-0 nuclei

The recent Amherst experiment was carried out by Robert Hilborn and his



Absorption of laser light passing through $^{16}O_2$, plotted as a function of the laser's detuning voltage. **a**: Scanning through the transition frequency for the Bose-allowed molecular rotation excitation from $K = 21$ to 22 yields a clear absorption signal. **b**: Scanning through the calculated frequency for the Bose-forbidden transition $K = 20$ to 21 yields only noise. Trying to fit an absorption curve produces a negative amplitude consistent with zero. (Adapted from ref. 3.)