

SEARCH AND DISCOVERY

New Measurements of Hydroxyl in the Middle Atmosphere Confound Chemical Models

The drive to measure, understand, and prevent ozone depletion over Antarctica has been so intense and attention-grabbing that the words “ozone” and “hole” now seem mated for life. But the ozone layer, which is densest at altitudes of 15–20 km, envelops the entire planet and extends into the mesosphere, where it plays a key role in the atmosphere’s physics and chemistry. Ozone molecules, heated by their absorption of ultraviolet photons from the Sun, provide most of the energy that drives circulation in the upper stratosphere and mesosphere. (Figure 1 depicts the vertical structure of the atmosphere.)

Ozone (O_3) forms in the same way throughout the atmosphere: Oxygen atoms, created when ultraviolet photons split O_2 molecules, bind with unsplit O_2 to form O_3 . Ozone destruction, however, varies with location. It’s most complicated over the poles, where winds, ice clouds, and low temperatures conspire with various chemical forms of chlorine, nitrogen, and bromine to destroy ozone. But above 40 km, ozone destruction is thought to be simple—uncomplicated by atmospheric effects and controlled predominantly by the so-called odd hydrogen species, HO_x , where $x = 0$ (atomic hydrogen), 1 (hydroxyl), or 2 (hydroperoxyl).

Despite this presumed simplicity, attempts in the early 1980s to predict the amount of ozone in the stratosphere underestimated the observed amount by 50–60%, a shortcoming that became known as the ozone deficit problem. Now, thanks to the steady effort of observers, lab scientists, and theorists, the gap between theory and observation has almost been closed.

By the middle of the 1990s, as atmospheric chemists gnawed away at the ozone deficit problem, a new problem sprouted: the HO_x dilemma. Standard chemical models can account for the amount of OH measured in the upper stratosphere (30–40 km) without any adjustments, but those same models must be signifi-

Nicknamed the atmospheric garbage disposal, the hydroxyl molecule is one of the most potent oxidizers throughout the atmosphere. Among its habitual targets is ozone.

cantly tweaked to fit the OH observations in the mesosphere (50–85 km).

The World Meteorological Organization’s fourth report on atmospheric ozone, published in 1998, concluded that the HO_x dilemma most likely arises from a difference in measurement technologies: balloon-based infrared spectroscopy up to 40 km (close to the maximum altitude that balloons can reach) and satellite-based ultraviolet spectroscopy above 50 km. But now, by extending the minimum altitude of satellite measurements to 38 km, the Naval Research Laboratory’s Bob Conway and company confirm¹ the balloon-based results² and their own previous

results from 50 km and higher.³ The origin of the HO_x dilemma seems to lie less with discrepant measurements than with insufficient models.

Correctly accounting for HO_x chemistry is important not only for ozone: “OH reacts with just about everything,” says New Mexico Tech’s Ken Minchwaner, “so it’s also important for cleansing the atmosphere of pollutants.” Furthermore, even though OH destroys ozone, it also reacts with the ozone-destroying chlorine monoxide and the more stable, less harmful hydrochloric acid, thereby regulating the relative abundances of malign and benign chlorine compounds.

Against a bright background

Hydroxyl in the middle atmosphere (mesosphere and stratosphere) is difficult to measure. Above 50 km, one of the molecule’s principal signatures is a band of lines around 308 nm emitted when ultraviolet photons from the Sun cause OH to fluoresce. Solar photons also Rayleigh-scatter off the atmosphere, forming a complex, feature-filled background against which the OH line has to be picked out. Compounding the difficulty is the low density of the middle atmosphere, which enfeebls all emission spectra.

To investigate the vertical distribution of OH (and, incidentally, nitric oxide) in the middle atmosphere, Conway’s team designed and built an instrument called the Middle Atmosphere High Resolution Spectrograph Investigation (MAHRSI for short). MAHRSI was one of the instruments aboard the CRISTA-SPAS satellite, which was deployed and retrieved by a space shuttle for two eight-day missions, in November 1994 and August 1997. Orbiting at an altitude of 304 km and an inclination of 57°, MAHRSI could observe the atmosphere between latitudes 52° S and 62° N. Figure 2 shows a picture of the satellite.

MAHRSI is a limb sounder—that is, an instrument that looks through the top of the atmosphere (“limb” is an astronomical term for the apparent

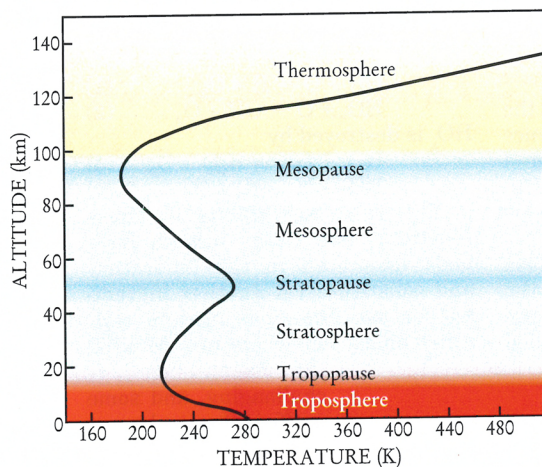


FIGURE 1. THERMAL STRUCTURE OF Earth’s atmosphere. The black line shows how the atmosphere’s temperature varies with altitude through the lower atmosphere (red), middle atmosphere (blue), and upper atmosphere (yellow). Monotonically changing temperature characterizes each of the atmosphere’s several spheres, which are separated by transition zones known as pauses. (The ionosphere, which starts in earnest at an altitude of about 80 km and extends into space, is not shown.)



FIGURE 2. THE CRISTA-SPAS satellite as seen from the bay of the space shuttle. (Courtesy of NASA.)

outer edge of a celestial body). For example, when MAHRSI observes a point 68 km directly above Earth's surface, its $0.01^\circ \times 1.15^\circ$ field of view encompasses a rectangular area at that point 0.3 km high and 34.4 km wide. Because the atmosphere's vertical structure follows Earth's curvature, the signal that MAHRSI detects originates from different altitudes. To derive the vertical OH profile, the altitude-integrated data have to be inverted under the assumption of spherical symmetry.

Another key assumption is that the brightness of the OH fluorescence lines is proportional to the number of OH molecules in the ground state. But photoexcited OH molecules can deexcite through collisions with O_2 and N_2 , as well as through fluorescence. This effect, which becomes large in the upper stratosphere, is included in the MAHRSI data analysis. Also included

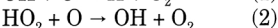
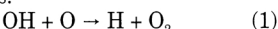
is the possibility that OH fluorescence is absorbed by ozone before it reaches the detector.

The concentration of OH depends not just on altitude but also on time of day, latitude, and longitude. As it speeds through the atmosphere, MAHRSI must therefore sample the OH profile quickly to avoid smearing the signal too much. In fact, MAHRSI takes just 151 seconds to complete a single vertical scan from 100 to 30 km.

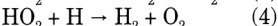
The right profile

One MAHRSI-observed OH profile is shown in figure 3, as are several model profiles. Typically, an atmospheric chemistry model incorporates hundreds of chemical reactions, as well as the measured distributions of long-lived species such as water vapor, which depend more on transport processes than on chemistry. Another key model ingredient is the solar illumination, which influences the chemical composition of the atmosphere through hundreds of photochemical reactions.

In the middle atmosphere, HO_x is created when water vapor and excited oxygen atoms combine to make OH. The relative concentrations of OH and HO_2 mainly depend on two reactions:



HO_x is destroyed by



The rate coefficients of these reactions, and many others, have been measured in the laboratory and constitute yet another ingredient of the chemical models that atmospheric scientists use. Making the measurements is challenging, and some coefficients are known to an accuracy no better than 50%.

Of the models represented in figure 3, only the one shown in blue incorporates canonical, laboratory-determined rate coefficients. It comes closest to fitting the data below 45 km, but uniformly overpredicts the OH concentration at higher altitudes. In their 1997 observations with the balloon-borne FIRS-2 instrument, Ken Jucks of the Harvard-Smithsonian Center for Astrophysics and colleagues found the same thing.²

The other models in the figure have been tweaked to fit the data above 50 km. The red model is the same as the standard model, but the rate coefficient for reaction 1 is half its laboratory-measured value. In the green model, the rate coefficient for reaction 2 is 20% lower and the rate coefficient for reaction 3 is 50% higher. But the tweaks, though successful at producing a good match above 50 km, cause the model to underpredict OH below 50 km.

What could be the source of the HO_x dilemma? It's not out of the question that the true values of key rate coefficients could lie outside their measured uncertainties. In the world of atmospheric chemistry, lab measurements are routinely reevaluated in the light of atmospheric data—sometimes resulting in better agreement.

The trouble is, it seems that no *single* set of rate coefficients, adjusted or not, can reproduce the measurements from the upper stratosphere, through the stratopause, and into the mesosphere. "It's as if the model just jumps the tracks at 45 km," says Conway's NRL colleague Dave Siskind. Siskind, Jucks, and others speculate that the models could be incomplete, missing certain key reactions because atmospheric chemists don't yet know about them.

One source of uncertainty is OH's partner in crime— HO_2 , which is just as destructive of ozone, but harder to measure. MAHRSI didn't measure HO_2 , but Jucks and company did. They found that, unlike the case for OH, standard chemistry overpredicts (by 25%) the concentration of HO_2 .

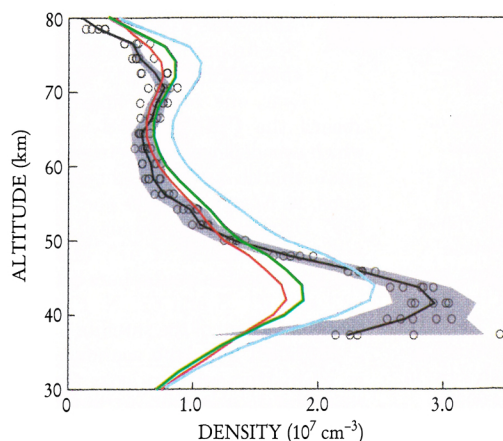


FIGURE 3. VERTICAL DISTRIBUTION OF OH as measured by the Middle Atmosphere High Resolution Spectrograph Investigation on 15 August 1997. The black line within the blue shaded area shows the average concentration of OH over the five-hour duration of the measurement period (the shaded area represents the uncertainty range; the circles represent one-hour averages). The colored lines represent the OH concentrations as predicted by various photochemical models: Blue corresponds to a so-called standard model based on the best available rate coefficients; red and green correspond to chemical models in which one or more rate coefficients have been adjusted to match the observations above 50 km. (Adapted from ref. 1.)

below 40 km. Says Jucks, "HO₂ observations in the mesosphere would be very important in solving the dilemma. They would give important clues about the balance of production and loss of HO_x, as well as the partitioning between OH and HO₂."

Water could yield another clue. During MAHRSI's first flight in 1994, the HALOE instrument on board the

UARS satellite measured the vertical distribution of water vapor.³ HALOE found two peaks in the H₂O distribution: one at 50 km that matches the OH distribution (see figure 3), and a smaller, unexpected peak at 65–70 km. "Since HO_x comes from water, maybe the funny water vapor distribution is tied to the HO_x problem," speculates Siskind, "but we're not

sure how. All we can say is that we don't know everything."

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References

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Chandra X-Ray Observatory Examines a New Kind of Black Hole

For decades, astronomers have been accumulating increasingly strong evidence for the existence of black holes in two distinct mass regimes: "stellar" black holes, weighing a few times the mass of the Sun ($M_{\odot}$), and "supermassive" black holes with masses ranging from 10^6 – $10^9 M_{\odot}$, always sitting at the centers of galaxies. There seemed to be nothing in between.

But last year, two groups of x-ray astronomers^{1,2} presented tentative suggestions of something quite new: a middleweight class of black holes much more massive than the stellar black holes but distinctly lighter than the supermassive giants. And now, a British-Japanese-US collaboration, availing itself of the new Chandra X-Ray Observatory, has presented the first strong evidence^{3,4} of such a middleweight black hole: sitting about 500 light-years off center in the nearby galaxy M82, with a mass of at least $500 M_{\odot}$. Its upper mass limit—perhaps $10^5 M_{\odot}$ —is somewhat more problematic.

The formation of stellar black holes is reasonably well understood. They seem, in all cases, to be the remnants of supernova explosions. But the formation of supermassive black holes at the centers of galaxies remains something of a puzzle. It's a chicken-and-egg problem: Do supermassive black holes act as seeds for galaxy formation, or is it the other way around?

The middleweight black holes have taken the theorists by surprise. Perhaps they result from some sort of runaway merger of stars in clusters of particularly large and dense stellar population. The study of such off-center middleweights, it is hoped, will improve our understanding of galaxy formation.

Chandra

NASA's Chandra x-ray telescope was launched into orbit in July 1999 (see *PHYSICS TODAY*, May, page 18). Its name honors the great theoretical

A surprising new class of middleweight black holes, perhaps 10 000 times more massive than the Sun, may have much to teach us about how galaxies form.

astrophysicist Subrahmanyan Chandrasekhar, who died in 1995.

The decisive capability that allowed Chandra to unmask the middleweight black hole in M82 is the extraordinarily fine angular resolution of the new telescope's x-ray optics (see figure 1) and its high-resolution imaging camera. The camera's sub-arcsecond resolution is an order-of-magnitude improvement on the older ASCA¹ and ROSAT² orbiting x-ray telescopes whose data yielded the earlier hints.

ASCA had provided the first hard-x-ray imaging observations of M82. In those data, Andrew Ptak and Richard Griffiths at Carnegie Mellon University called attention to an unusually bright and variable x-ray source within about 10 arcseconds of the galaxy's

center.¹ With ASCA's angular resolution, they could not determine whether the source might be off center. Nor could they verify that it was a single compact source. But Ptak and Griffiths argued that the x rays were being produced by the accretion of surrounding material onto a black hole with a mass of at least $450 M_{\odot}$.

Examining the ROSAT and ASCA data from 39 nearby galaxies (not including M82), Edward Colbert and Richard Mushotsky at NASA's Goddard Space Flight Center had reported evidence of middleweight black holes near the centers of three spiral galaxies.²

A closer look at M82

The flamboyant M82, because of its evident star-forming hyperactivity, is classified as a "starburst galaxy." There is no optical evidence of a supermassive black hole at its center. Chandra observed M82 for 10 hours on 28 October 1999, and then for another 5 hours on 20 January.

To study the Chandra observations

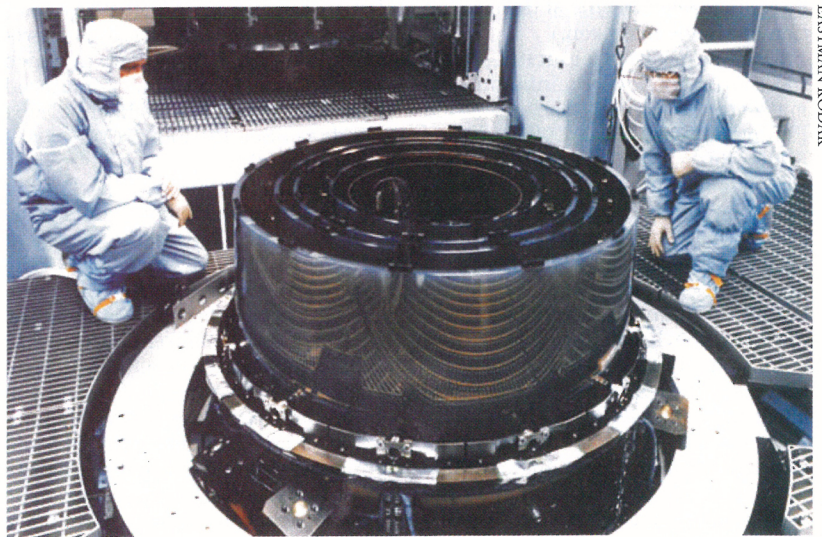


FIGURE 1. HIGH-RESOLUTION MIRROR ASSEMBLY of the Chandra X-Ray Observatory at Eastman Kodak before completion. The orbiting telescope's optics employ a nested set of four barrel-shaped mirrors that reflect incident x rays at glancing angles.