

energies of the nominally degenerate states that cause their energies to differ slightly. These corrections are calculable in quantum electrodynamics as coefficients in a series expansion in powers of a small quantity called the fine structure constant, although several effects may contribute to a particular order in the expansion.

The ultraviolet emission recorded by the Brandeis scientists corresponded to the decay from an excited state at  $n = 2$  to the ground state at  $n = 1$ . To further characterize the  $n = 2$  excited state, the investigators attempted to examine its fine structure, that is, the energy difference between two different quantum states with  $n = 2$ . To make this fine structure measurement, a radio frequency resonant cavity was constructed at the target chamber. Then, when microwave radiation of the appropriate frequency to cause a transition from an  $n = 2$  state with zero orbital angular momentum (called the  $2S$  state) to another with a nonzero momentum (called the  $2P$  state) was introduced into the cavity, they found about a 10 percent increase in the ultraviolet emission that satisfied the criterion for coinciding with gamma rays. The increased ultraviolet emission is in accordance with quantum mechanical selection rules that prohibit direct transitions between two states both with zero orbital angular momentum, such as the ground state ( $1S$ ) and some excited states ( $2S$ ). The

microwave frequency needed to cause the increased coincidence rate was  $8628.4 \pm 2.8$  megahertz which is within 10 megahertz of the theoretical value calculated from quantum electrodynamics by Thomas Fulton (now at Johns Hopkins University) and Paul C. Martin of Harvard University in 1954.

Predictions stemming from quantum electrodynamics have been extensively and accurately tested in a wide variety of physical phenomena at the atomic level, with remarkable agreement between theory and experiment in every case. In the face of such spectacular success, there has arisen a widespread feeling that, at least at low energies, quantum electrodynamics is for all intents and purposes a satisfactory theory. Nonetheless, scientists say there are important reasons for looking to experiments on positronium to provide further confirmation of quantum electrodynamics and that make it likely that the Brandeis experiments will stimulate further attempts at precision measurements of the excited states of positronium.

For example, some of the tests of quantum electrodynamics involve precision measurements of small corrections to the energy levels of hydrogen and other simple atoms, such as the hyperfine splitting of the  $1S$  ground state (due to the interaction of the magnetic moments of the nucleus and the electron in the case of hydrogen) and

the Lamb shift (the difference in energy between the nominally degenerate  $2S$  and  $2P$  excited states). Agreement between theoretical and experimental values of these minute energy differences exists to several significant figures.

Complicating such tests, however, is the presence of the atomic nucleus. The nucleus itself has a structure, and effects arising from the nuclear structure can make small contributions to these energy differences. In positronium, moreover, there are additional effects which do not occur in atomic systems with nuclei. Thus, the study of positronium affords an opportunity to fully test quantum electrodynamics without the presence of complicating nuclear effects.

The fine structure measured at Brandeis agrees with that calculated through the third significant figure, but contributions from as yet uncalculated terms in the theory, as estimated by Fulton and Martin, are expected to be comparable to the present experimental uncertainties. According to Berko, a number of improvements and additional measurements would need to be carried out in order to increase the precision of the fine structure determination. Such improvements are likely to be made and precision measurements carried out in the future. As it stands, the Brandeis result is as precise as the theory with which it can be compared.—ARTHUR L. ROBINSON

## Air Pollution: Where Do Hydrocarbons Come From?

Man's knowledge about air pollution and its causes is limited. Despite the laws that have been enacted to curtail emissions of potential pollutants from automobiles, for example, the role of automobile emissions in the genesis of the most severe forms of pollution, including photochemical smog, is incompletely understood. The lack of knowledge about this subject was recently illustrated by the controversy surrounding a report which concluded that, in certain areas and under certain conditions, hydrocarbons released from trees and other vegetation may be more important than those released from automobiles in the initiation of smog.

This possibility, which is based on very preliminary results obtained from limited data, has been sharply criticized by many investigators who have argued—largely on the basis of intuition—that the hypothesis cannot be correct. But the sad fact of the controversy is that there is not enough background information either to support or to refute the hypothesis.

The contested study was performed by

Raymond A. Saunders, Fred E. Saalfeld, and J. R. Griffith of the Naval Research Laboratory in Washington, D.C. The three investigators do not normally work in the field of air pollution research, a fact which has further fueled the controversy surrounding their conclusions. Their findings were a serendipitous result of their attempts to measure the concentrations of dissolved gases and hydrocarbons in ocean water. They developed a sophisticated gas chromatograph-mass spectrometer system for detecting and identifying the compounds and were refining the technique using water samples from local sources. On the spur of the moment, they decided to collect water samples from a rainstorm on 13 August 1973 that ended a period of intense smog in Washington.

They found that the rainwater contained unusually high concentrations of the cyclic ether 3-methylfuran; its concentration was, in fact, more than 100 times as great as that of any other hydrocarbon in the water. 3-Methylfuran is a relatively reactive substance that accounts for no more than

about 0.3 percent of the hydrocarbons in automobile emissions. Saunders thus suggests that the most likely source of the 3-methylfuran he observed is the atmospheric oxidation of terpenes that are released by trees and other vegetation, particularly during late summer. This oxidation, in turn, could contribute to the formation of smog-producing ozone by interfering with the natural cycle of oxygen and oxides of nitrogen.

In the absence of hydrocarbons, both oxygen and nitrogen dioxide in the atmosphere are in a rough equilibrium with ozone and nitric oxide. Nitrogen dioxide ( $\text{NO}_2$ ) in the presence of sunlight is dissociated into nitric oxide ( $\text{NO}$ ) and an atom of oxygen; the atom of oxygen then combines with a molecule of oxygen to form ozone. The ozone can then react with nitric oxide to re-form nitrogen dioxide, even in the dark. When several different hydrocarbons are present, however, they are converted by an incompletely understood mechanism to highly reactive peroxy compounds. These peroxy compounds in-

terfere with the nitrogen-oxygen cycle by oxidizing nitric oxide to nitrogen dioxide, thereby preventing the destruction of ozone and allowing it to accumulate to higher than normal concentrations.

Saunders thus suggests that in certain areas—such as Washington, where there are few sources of hydrocarbons other than automobiles—and at certain times of the year, hydrocarbons produced by vegetation could, with the proper atmospheric conditions, be the primary contributor to the formation of photochemical smog. The best example of this process, he suggests, might be found in the Appalachian Mountains near Washington, which are also known as the Great Smokies because they are and have always been covered by a smoglike haze during most of the summer and early fall. This haze conceivably results from hydrocarbon emissions from the forests covering the mountains, although this hypothesis has not been proved.

Support for the thesis that automobiles are not always the primary source of the hydrocarbons that initiate smog formation was recently provided by Alan R. Bandy of Old Dominion University. Bandy measured the concentration of atmospheric pollutants in the Tidewater area (near Norfolk) of Virginia, using gas chromatographic techniques comparable to those used by the Environmental Protection Agency (EPA) in its studies of other cities. He used the hydrocarbon acetylene as a tracer because, so far as is known, atmospheric acetylene is produced only by combustion. He measured the ratio of the concentration of all other hydrocarbons in the atmosphere to the concentration of acetylene and compared that ratio to the ratio characteristic of automobile exhaust.

With this technique, Bandy found that, during certain periods of the summer, the Tidewater atmosphere contained as much as eight times the concentration of low-molecular-weight saturated hydrocarbons (those with six carbons or fewer) that would be expected if automobiles were the primary source of hydrocarbons. He also found that the Tidewater atmosphere contained substantially lower concentrations of other pollutants, such as carbon monoxide and oxides of nitrogen, than were observed in cities with comparable concentrations of photochemical oxidants. He thus concludes that, at the time of the measurements, automobiles were not the primary source of the hydrocarbons that contributed to the formation of photochemical oxidants. Bandy was not able to identify the source of the hydrocarbons; but he suggests that evaporation from industrial and military storage tanks in the area is a more likely source than vegetation.

Many air pollution scientists have sharp-

ly criticized the results of Saunders and his associates on several grounds. Foremost among these, according to Joseph J. Bufalini of EPA, is the fact that Saunders' conclusion—and to a lesser extent, that of Bandy—seems to contradict everything that has been learned about air pollution to date. Studies by EPA of several cities, such as Los Angeles, St. Louis, Phoenix, and Houston, have shown conclusively that the primary source of hydrocarbon pollutants is automobile emissions, although evaporative emissions may be a large contributor. Bufalini thus argues that the situation should be similar in Washington and the Tidewater area, even though EPA has not measured pollutants in those areas. But Saunders argues that most of the EPA studies have been conducted in western and midwestern cities, where there is not nearly as much vegetation as along the East Coast.

A second objection, according to Reinhold Rasmussen of Washington State University, is that Saunders' postulated mechanism for formation of 3-methylfuran seems highly unlikely on the basis of current knowledge of the reactions of terpenes. And even if the reaction did occur, he adds, the atmospheric oxidation of terpenes produces such a large quantity of products that it is unlikely that any one product would predominate in the manner suggested by Saunders. Furthermore, Bufalini adds, 3-methylfuran is so reactive that, even if it were formed, it would probably decompose before it could accumulate in large quantities.

#### Only One Data Point

Perhaps the most important objection to the results of Saunders and his associates, however, is that the conclusions are based on only one data point—water collected during one storm that ended one smog incident. Saunders readily concedes the insufficiency of the data and raises further reservations of his own. He points out, for example, that a rain storm might not necessarily be a good way of sampling the atmosphere. The rain was presumably initiated by the movement of a pressure front into the Washington area, so it is conceivable that the hydrocarbons actually present in Washington were blown away before the rain began. Monitoring data for the area, unfortunately, is insufficient to determine when hydrocarbons disappeared from the atmosphere in relation to the beginning of the storm.

Another problem, Saunders notes, is that little is known about the initiation of rainstorms. It is possible, for example, that condensation nuclei of the raindrops were formed elsewhere and that the concentration of hydrocarbons in the rain re-

flects their concentrations at that site. It is also possible that molecules of 3-methylfuran or aerosols containing the chemical might somehow preferentially serve as condensation nuclei. Saunders, in fact, admits to being somewhat uncomfortable about the attention his results have received because there are so many reservations about the significance of the data and because of its preliminary nature. The only reason he published the data in this form, he argues, is so that it might serve as a "point of departure" for further work.

Despite the controversy over Saunders' conclusions, it is becoming increasingly clear that there may be many natural sources of hydrocarbons that can stimulate the formation of photochemical oxidants. Several investigators, such as Lyman A. Ripperton of the Research Triangle Institute and Peter E. Coffey and William N. Stasiuk of the New York State Department of Environmental Conservation, have shown that unusually high concentrations of ozone can be found in many rural areas where there appear to be few man-made sources of hydrocarbons to stimulate its formation. The source of the ozone is unknown.

Last month, Rasmussen reported that he had measured significant quantities of hydrocarbons in the atmosphere over equatorial portions of the Pacific Ocean far from land. The concentration of hydrocarbons, though low, was sufficient to stimulate the formation of ozone when oxides of nitrogen—which were not present at the location—were added to atmospheric samples in a chamber exposed to sunlight.

It has long been known, furthermore, that methane and other simple hydrocarbons arising from the decomposition of vegetation are present in the atmosphere in significant quantities during certain times of the year. It had been assumed that these simple hydrocarbons are too unreactive to produce significant quantities of ozone; but Ripperton, among others, has suggested that simple hydrocarbons will produce ozone if trapped in air masses for long periods of time. Thus it is beginning to seem quite difficult to attribute all of the formation of photochemical oxidants to automobile and industrial emissions.

One further conclusion may be drawn from the uncertainties surrounding the results of Saunders and of Bandy. The relatively unsophisticated monitoring of pollutant concentrations conducted by many localities may be of some value in determining periods of hazard from high concentrations of pollutants. It will rarely, however, be of value in identifying the sources and fates of the pollutants.

—THOMAS H. MAUGH II