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

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.

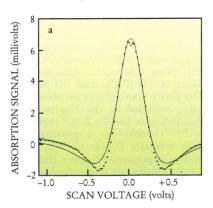
The Pauli exclusion principle makes it possible for experimenters to test the Fermi-Dirac statistics of electrons with awesome precision. By looking for x rays from injected electrons falling into already occupied inner orbitals in a strip of copper, Eric Ramberg and George Snow at Maryland were able to show in 1990 that, at most, one or two electrons in 10²⁶ dared violate the exclusion principle.

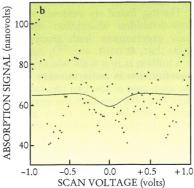
Bose-Einstein statistics, however, don't offer the experimenter anything quite as convenient as the exclusion principle. Only now, with the appearance of two papers, back to back, in a recent issue of Physical Review Letters, do we have the first high-precision tests of identical-particle statistics for bosons.^{2,3} Exploiting the extremely stable tunable diode lasers that have

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

been available only in the last few years, groups at the University of Naples² and Amherst College³ 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 ¹⁶O₂, 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 16O2 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 conjectured4 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 ¹⁶O₂, 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 $\hat{K} = 20$ to 21 yields only noise. Trying to fit an absorption curve produces a negative amplitude consistent with zero. (Adapted from ref. 3.)

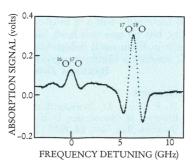
student Candice Yuca. "Td been thinking for a long time about how I could do a precision test of the symmetrization postulate for bosons," Hilborn told us. "I did some preliminary experiments with molecular rotation spectra in 1990, but they didn't turn out very well. Then, about four years ago, these very stable semiconductor diode lasers came along with just the right wavelengths for $\rm O_2$, and I knew it could, and therefore should, be done."

Hilborn's experiment is very similar to the experiment done independently. at about the same time, by Guglielmo Tino and colleagues at the University of Naples. Both groups used absorption spectroscopy to look for evidence of transitions from the electronic ground state of ${\rm ^{16}O_{2}}$ in Bose-forbidden even-K molecular rotation states to odd-K excited states with an electronic wavefunction that is symmetric under exchange of the nuclei. Such transitions are prohibited by the symmetrization postulate, but not by the ironclad "superselection rule" that absolutely forbids transitions between states whose total wavefunctions (elec $tronic \times rotational \times vibrational...)$ have opposite overall exchange symmetry, irrespective of any violation of Bose statistics.

Oxygen was an attractive choice because the zero spin of its principal isotope, ¹⁶O, and the low abundance of the other isotopes make the interpretation of the data relatively easy. Furthermore, because oxygen atoms are quite light, the spacing between molecular rotation levels is conveniently wide.

With a tunable diode-laser beam passing repeatedly through an oxygen absorption cell on its way to a photon detector, each group searched for magnetic-dipole transitions from Bose-forbidden even-K electronic ground states to K+1 states over a range of Ks in the so-called A band, around 762 nm in the far red. Using molecular parameters determined from the known transitions in this band, one can calculate with great precision what the frequencies of the Bose-forbidden absorption lines would be if they exist. The Bose-forbidden transition from K = 20 to 21, for example, would appear at 391 159.4 GHz, just 141.9 GHz above the allowed transition from K = 21 to 22.

Coarse frequency tuning of the diode lasers is done by adjusting the temperature, and then one fine-tunes by varying the diode current. To look sensitively for a particular absorption line, the experimenters modulated the laser's output frequency at a few kilohertz, sweeping it repeatedly back and forth across the transition frequency



DIFFERENT ISOTOPES in an O_2 molecule free the spectrum from the prohibitions of identical-particle statistics. The small natural abundance of $^{16}O^{17}O$ molecules produces an absorption signal for the rotational transition from K=2 to 3, which is forbidden to $^{16}O_2$ by Bose statistics. (Adapted from ref. 2.)

in question and using a lock-in amplifier to bring out any absorption signal at twice the modulation frequency. This kind of lock-in detection is a standard technique for filtering out noise.

The figure on page 19 shows the result of a typical search by Hilborn and Yuca. For the Bose-allowed magnetic-dipole excitation from K=21 to 22, they saw a strong absorption line; but for the Bose-forbidden excitation from K=20 to 21, they saw nothing but noise.

Nonidentical isotopes

If, however, the two oxygen nuclei in the molecule are different isotopes, the prohibitions of identical-particle statistics no longer apply. The oxygen in the absorption cells has the natural abundance of ¹⁸O (0.2%) and ¹⁷O (0.04%). The figure above shows an absorption curve recorded by the Naples group that indicates the K = 2 to 3 excitation in ¹⁶O¹⁷O molecules, a transition that Bose statistics forbids in ${}^{16}O_2$. This isotope dependence is more than just a good illustration of identical-particle effects at work in the quantum realm. It also helps calibrate the sensitivity of the experiments.

Having found no evidence of any Bose-forbidden absorption lines in their experiments, both groups conclude that, at most, one ¹⁶O₂ molecule in a million is in a state whose overall wavefunction is antisymmetric under the exchange of the two identical nuclei. Thus they confirm the symmetrization postulate with much greater sensitivity than any previous test with spin-zero nuclei. These experiments are also, in effect, tests of the Fermi statistics of the protons and neutrons that make up the nuclei. "We're testing the validity of the spin-statistics

connection for composite particles," Tino told us.

"Such precision tests are worth doing," says Greenberg, "even though there's no fully satisfactory theoretical framework for small violations of the symmetrization postulate. At best, you'd have to give up local commutativity of observables. But such nonlocal field theories could at least preserve relativistic kinematics."

On the other hand, large, discrete violations of the symmetrization postulate can generally be recast in terms of hidden degrees of freedom. That's what happened in the early days of the quark model, when some of the baryon states appeared to violate the Fermi statistics of spin-1/2 quarks. Greenberg pointed out in 1964 that the paradox would be resolved if quarks were not ordinary fermions, but rather "parafermions" that could be bound together in exchange-symmetric three-quark states. This kind of parastatistics has much the same effect as the subsequent introduction of the hidden variable "color," which was to become the central feature of quantum chromodynamics, the now standard theory of the strong interactions.

Dmitry Budker and coworkers at the University of California, Berkeley, are preparing to test the symmetrization postulate for photons, which are spin-1 bosons, by attempting to induce Bose-forbidden two-photon excitations in atomic states with a Ti:sapphire laser

The striking difference between the rotation spectra of ¹⁶O₂ and ¹⁶O¹⁷O, which goes far beyond trivial isotope effects and has now been tested to a part in a million, points up the amazing consequences of identical-particle indistinguishability in quantum phenomena. Candice Yuca was an Amherst undergraduate, majoring in philosophy as well as physics, when she did the experiment with Hilborn. Half of her senior honors thesis, which describes the experiment, deals with philosophical issues raised by the concept of indistinguishability. She is now a physics graduate student at the University of Cambridge in England.

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