manner. It is indeed surprising that ozone molecules of mass 51 amu either can carry a large enrichment of nearly 20% or can be depleted by a few percent depending on the oxygen atoms and molecules from which they were formed. Kaye (*8*) used conventional recombination theory based on approximate unimolecular rate theory and statistical thermodynamics to derive the ozone isotope distribution. His results show a mass-dependent depletion in all heavy isotopes, which is only observed in the two completely symmetrical molecules (see figure).

Despite the fact that much experimental information is at hand, the isotopic anomaly has lacked plausible explanations. A fair number of attempts have been made (*6*, *9*), but so far they have been unable to explain all of the experimental results. Most recently, Anderson *et al.* (*10*) proposed that metastable states in the ozone molecule may be responsible for the symmetry-controlled isotope effect that has been observed in other molecules. Metastable electronic states of ozone have been found, but the connection to the isotope anomaly has not been made. The lifetime of the metastable molecule will be of critical importance.

The work of Gellene (*1*) now permits a quantitative prediction of the isotope fractionation pattern in the ozone formation process. The theory is able to reproduce the general features of the isotope distribution shown in the figure. The new permutation inversion symmetry scheme developed by Gellene and co-workers, taking into account nuclear symmetrization in reactive collisions, is particularly well suited for determining the effects of isotopic substitution in gas-phase collision processes. In contrast to the mass-dependent kinetic isotope effects well known in reaction dynamics, the unusually large isotope effects recently found by Gellene in his laboratory experiments [references in (*1*)] have been explainable in terms of the new symmetry correlation scheme, lending credibility to the new approach.

The jury is still out on which explanation will best describe the ozone isotope enrichments. In particular, the subtle effects seen in the symmetrical and asymmetrical variety of isotopomers wait for a solution. Compared to the laboratory and tropospheric results, the stratospheric data show often very high abundances of heavy ozone. Gellene's theory, in principle, has the potential to explain such large and variable isotope enrichments. Other processes such as symmetry selection through metastable states (*10*) or reactions involving highly vibrationally excited O_2 (*11*) are still competing to be the correct explanation of the ozone isotope effect; future experiments will have the task of proving one or the other to be the right explanation.

References

1. G. I. Gellene, *Science* **274**, 1344 (1996).
2. K. Mauersberger, *Geophys. Res. Lett.* **8**, 935 (1981); *ibid.* **14**, 80 (1987).
3. B. Schueler, J. Morton, K. Mauersberger, *ibid.* **17**, 1295 (1990).
4. A. Meier and J. Notholt, *ibid.* **23**, 551 (1996); F. W. Irion *et al.*, *ibid.*, p. 2377.
5. D. Krankowsky *et al.*, *ibid.* **22**, 1713 (1995).
6. J. E. Heidenreich and M. H. Thiemens, *J. Chem. Phys.* **84**, 2129 (1986).
7. K. Mauersberger, J. Morton, B. Schueler, J. Stehr, *Geophys. Res. Lett.* **20**, 1031 (1993).
8. J. A. Kaye, *J. Geophys. Res.* **91**, 7865 (1986).
9. J. E. Heidenreich and M. H. Thiemens, *J. Chem. Phys.* **78**, 892 (1983); J. J. Valentini, *ibid.* **86**, 6757 (1987); W. L. Morgan and D. R. Bates, *Planet. Space Sci.* **40**, 1573 (1992).
10. S. M. Anderson, K. Mauersberger, J. Morton, B. Schueler, *ACS Symp. Ser.* **502**, 155 (1992).
11. P. L. Houston, A. G. Suits, R. Toumi, *J. Geophys. Res.* **101**, 18892 (1996).

NOTA BENE: PHOTOPHYSICS

The 110% Solution

Supersaturated solutions contain more dissolved substance than the solvent can normally carry. As a result, they are on the verge of crystallizing; all that is needed is a seed or trigger to provide a nucleus for crystal formation. A familiar example is rock candy, which crystallizes onto a string dipped in sugar water. In the 1860s, John Tyndall studied the condensation of supersaturated vapors triggered by light (*1*). A dramatic form of light-induced precipitation was discovered in the 1970s by researchers at Princeton. When they passed a laser beam through sodium vapor, they observed laser "snow" (*2*) as the sodium atoms clustered and precipitated. In this and other cases of laser-induced nucleation of supersaturated solutions, the light produced a chemical change causing crystallization or precipitation. However, as recently reported in *Physical Review Letters*, Garetz *et al.* have now observed the photonucleation of supersaturated urea solution—but without a photochemical change (*3*).

Urea is well known to laser physicists because it has important nonlinear optical properties. Garetz *et al.* were investigating whether the nonlinear process of second harmonic generation, whereby laser light can be converted to light at twice the optical frequency, could be observed in aqueous solutions of urea. The solutions had concentration ratios c/c_{sat} between 1.10 and 1.29, where c_{sat} is the solubility of urea, and so were highly supersaturated. The incident laser light was at a wavelength of 1.06 μm, with a pulse duration of 20 ns and a pulse power intensity of 250 MW/cm^2. At this intensity, the laser pulses caused nucleation of the urea solution as a single small crystallite, followed by crystallization of the entire sample.

In contrast to previous examples of photonucleation, the authors believe that the crystallization occurred by an entirely nonphotochemical process. It is conceivable that the laser could have photolyzed some impurity, but the samples were carefully prepared to be pure and free of dust. Urea itself has no absorption bands at the infrared laser wavelength, so a direct light-induced chemical reaction is unlikely, as is some process involving the absorption of multiple photons. The authors also checked for chemical production of nucleation centers by redissolving the crystallized urea and saw that they could re-create the supersaturation. Thermal effects were discounted because heating would make the solution more, not less, stable.

One key characteristic implicated the electric field produced by the laser as the cause of the crystallization: The urea crystals that formed by laser action were oriented along the polarization direction of the light. This orientation suggests a kind of electric field–induced alignment of the molecules known in other contexts as the optical Kerr effect. Kerr effect optical shutters use electric fields to change the optical polarizing properties of liquids and are used in high-speed movie cameras to record projectile motion or the time evolution of explosions. Garetz *et al.* speculate that the Kerr effect assists the formation of nucleation sites by aligning existing prenucleating clusters that normally form and break up continually in solution.

Although more work will be needed to confirm this picture, the light-induced crystallization of solutions may offer ways to study the fundamental physics of nucleation and might provide a method for cleanly and controllably inducing the crystal formation of technologically useful substances.

—**David Voss**

References

1. J. Tyndall, *Philos. Mag.* **37**, 384 (1869).
2. A. Tam, G. Moe, W. Happer, *Phys. Rev. Lett.* **35**, 1630 (1975).
3. B. Garetz *et al.*, *ibid.* **77**, 3475 (1996).