ticipants, even though such awareness is not necessary for delay conditioning to occur. Interestingly, a similar pattern has been observed during eyeblink conditioning in the rabbit where, as noted by the authors, delay conditioning is accompanied by hippocampal cell activity—even though hippocampal lesions do not abolish delay conditioning. Might such activity indicate some form of incidental awareness in the conditioned animals? In view of the fact that trace conditioning in the rabbit is impaired after hippocampal lesions, and the observed dependence of trace conditioning on awareness in humans, Clark and Squire's results raise the intriguing possibility that delay and trace conditioning could be used to study aspects of awareness in nonhuman animals.

Data from conditioning experiments in humans in some respects parallel earlier findings from priming experiments and a different type of awareness. After studying a list of common words (for example, *garden*), amnesic patients show intact priming of the studied items when asked to complete three-letter word stems (*gar__*) with the first word that comes to mind (5). The magnitude of this word-priming effect in healthy participants who become aware during the test that they are producing words from the study list and those who do not (6). In contrast, in a variation of this test amnesic patients exhibit impaired priming of new associations between unrelated words (3, 6). For example, after studying an unrelated word pair (for example, *shirt-garden*), healthy volunteers—but not severely amnesic patients—are more likely to complete the word stem "*gar__*" with "*garden*" when the stem is paired with "*shirt*" than when it is paired with another unrelated word from the study list. However, healthy volunteers tested under similar conditions exhibit priming of new associations on the test only when they are aware that they are producing words from the study list (6). Thus, just as awareness of the relation between tone and air puff appears necessary for trace conditioning, awareness of the relation between study and test appears necessary for associative priming of stem completion. Both phenomena depend on the medial temporal lobe system that is damaged in amnesia.

During word priming, neural activity is reduced in regions of extrastriate visual cortex involved in perceptual analysis and in regions of left inferior frontal cortex involved in conceptual analysis (3, 7). Surprisingly, one study that used the stem completion task also reported a small increase in medial temporal lobe activity during word priming (8). However, this activation likely occurred because participants spontaneously became aware that they were completing stems with words they had studied earlier (9).

Awareness has also emerged as a central issue in sequence learning, in which people respond rapidly to a series of visual stimuli that appear in various locations on a screen. Participants are unaware that the series contains a recurring sequential pattern, but both healthy volunteers and amnesic patients learn the pattern (10). Neuroimaging studies reveal consistent activations of motor cortex and basal ganglia during sequence learning (10). Several brain regions (left premotor area, left anterior cingulate, and right ventral striatum) showed increased activity when the sequence was changed across trials—even though participants were unaware of the change (11). Thus, neuroimaging data are consistent with the idea that sequence learning without awareness relies on brain regions outside the medial temporal region (10).

Evidence from the three types of learning—classical conditioning, priming, and sequence learning—converges on the conclusion that several phenomena of memory and learning that do not require the medial temporal region also do not require particular types of awareness (see figure). Defining and measuring awareness presents a formidable challenge (12). Nonetheless, by contrasting "unaware" expressions of memory with situations in which awareness does play a vital role, and by combining data from brain-injured patients, neuroimaging studies, and even nonhuman animals, it should be possible to gain even greater insight into the neural processes that support memory, learning, and awareness (see figure).

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13. Supported by National Institute on Aging grant AG08441.

ATMOSPHERIC CHEMISTRY

Photochemistry of Ozone: Surprises and Recent Lessons

A. R. Ravishankara, G. Hancock, M. Kawasaki, Y. Matsumi

The highly reactive hydroxyl radical OH is nature's atmospheric detergent; among other things, it initiates the oxidation of pollutants, cleansing them from the atmosphere. Hydroxyl formation in the lower atmosphere begins with the solar photolysis of ozone, which produces the electronically excited oxygen atom $O(^1D)$. In general, the reactions of electronically excited species are of negligible importance in the chemistry of the lower atmosphere, but the case of $O(^1D)$ is a notable exception: Its role is pivotal. Even though most of the $O(^1D)$ is deactivated to the ground state, $O(^3P)$, the small fraction that survives to react with H_2O and CH_4, turns out to be the major source of OH. Knowledge of how $O(^1D)$ is formed in the atmosphere is therefore critical in understanding the creation of OH. Recent surprising findings from several laboratories, including our own, are beginning to reveal the importance of the longer wavelength "tail" in the chemistry of $O(^1D)$ formation. The longer wavelengths are important because stratospheric ozone screens most of the shortwave ultraviolet from the lower atmosphere.

The weakness of the chemical bond in ozone and the existence of low-lying electronically excited states of both atomic and molecular oxygen lead to a number of energetically allowed dissociation channels. The

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A. R. Ravishankara is in the Atmospheric Chemical Kinetics Program, Aeronomy Laboratory, National Oceanic and Atmospheric Administration, Boulder, CO 80303, USA; G. Hancock is in the Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford OX1 2QZ, UK; M. Kawasaki is in the Department of Molecular Engineering, Kyoto University, Kyoto 606-8501, Japan; Y. Matsumi is at the Solar Terrestrial Environmental Laboratory and Graduate School of Science, Nagoya University, 3-13, Honohara, Toyokawa 442-8507, Japan. E-mail: ravi@al.noaa.gov

most important channel is the reaction

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^1\Delta) \tag{1}$$

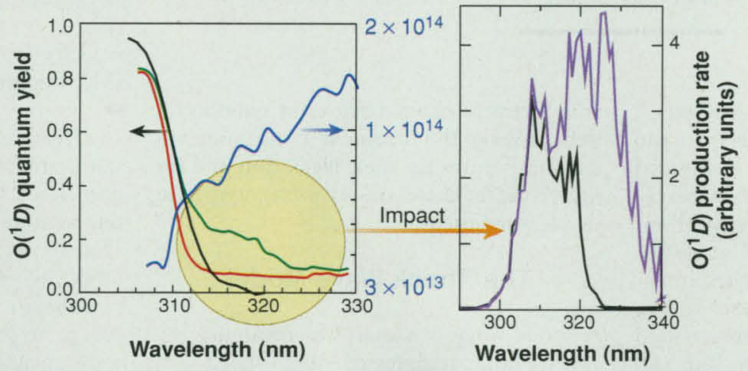
which has a photon energy threshold at 310 nm and forms two excited products, an unusual result in any chemical reaction. The other known process is the reaction

$$O_3 + h\nu \rightarrow O(^3P) + O_2(^3\Sigma) \tag{2}$$

which results in ground-state products. If dissociation to form $O(^1D)$ is to take place at longer wavelengths [where the solar flux is much higher (see figure)], it can only occur by the formation of an unexcited oxygen molecular partner, as in the reaction

$$O_3 + h\nu \rightarrow O(^1D) + O_2(^3\Sigma) \tag{3}$$

or by photolysis of internally excited ozone molecules. Both such processes have in the past been considered to be of negligible importance. Reaction 3 to form $O(^1D)$ and ground state O_2 is "spin forbidden," a quantum mechanical concept in which processes that do not conserve electron spin are deemed unlikely, particularly in molecules such as ozone, which contain only light atoms. Furthermore, at room temperature only a small fraction of ozone molecules possess enough internal energy to allow them to be dissociated in the "spin allowed" process (reaction 1), and in the past, its contribution to the $O(^1D)$ yield was considered to be negligible. On the basis of these arguments, the yield of $O(^1D)$ at wavelengths greater than the 310-nm threshold was neglected.



A wag of the tail. (**Left**) The variation of the quantum yield for the production of $O(^1D)$ in the photodissociation of O_3 with wavelength at ~200 K (red) and ~250 K (green), derived from recent studies (*4*). The black line is that recommended previously by data evaluation panels (*3*). The increase in photon flux (photons per square centimeter per nanometer of wavelength per second) is shown by the blue curve. Note that the photon flux is plotted on a logarithmic scale. (**Right**) The impact of $O(^1D)$ formation by way of the spin-forbidden channel and vibrationally excited ozone is shown as $O(^1D)$ production rate with wavelength for an altitude of 20 km, solar zenith angle of 85° with 250 Dobson units of overhead ozone. The purple curve includes the contribution of these two processes, and the black one (from previous recommendations) does not, showing the importance of these two processes.

In the 1990s, ozone photodissociation experiments were started, in which the fragments of dissociation were observed directly, by techniques adapted from chemical physics studies (*1*). These studies showed a definite, nonnegligible yield at longer wavelengths, an effect that had already been observed and considered (*2*), but had been discarded as being untenable (*3*). In a number of experiments carried out in our (*1*, *4*) and other laboratories (*5*), all of the energetically allowed fragments of importance were observed [the results for $O(^1D)$ are shown in the figure]. There is a marked "tail" in the $O(^1D)$ quantum yields [the fraction of ozone molecules that dissociate to give $O(^1D)$ upon absorption of one photon] that extends to at least 330 nm and is highly temperature-dependent. These detailed studies have produced a picture that is nearly complete, at least for atmospheric purposes. Above 310 nm, there are important contributions to $O(^1D)$ production from internally excited ozone as well as the spin-forbidden pathway (reaction 3), both processes that were previously thought to be negligible (*3*). Now, to complete the picture, even the reaction

$$O_3 + h\nu \rightarrow O(^3P) + O_2(^1\Delta) \tag{4}$$

has been observed. Internally excited ozone molecules strongly absorb radiation at longer wavelengths to reach the excited state responsible for dissociation in reaction 1 and efficiently channel their internal energy toward breaking the ozone bond. This mechanism explains the marked temperature dependence seen in the data: At low temperatures, there are simply not enough ozone molecules present in the internally excited levels. This effect should become less important as the wavelength is increased, precisely as seen in the data. However, this is not the full story: As the figure shows, there is a persistent contribution even at the lowest temperatures (red curve in the left panel), which appears to be approximately invariant with wavelength. Measurements in which the kinetic energies of the products have been directly determined have shown this effect to be the result of the spin-forbidden step (reaction 3).

Researchers in chemical physics have developed methodologies for studying photodissociation processes, and these have turned out to be very useful in problems of atmospheric importance. The ability of these techniques to unravel complex photodissociation dynamics has been crucial: A key point is that the dissociation of internally excited species and spin-forbidden processes, exotic as they may sound, are occurring in something as globally and socially important as the atmosphere. The figure shows the rate of production of $O(^1D)$ (and hence OH) as a function of wavelength, and it is clear that in many situations, its formation at wavelengths above the 310-nm threshold is highly significant. We find that it could enhance the balance of OH formation, particularly at high latitudes in the troposphere from late autumn to early spring. This change will affect the lifetime of short-lived species such as CO, a common pollutant, and also control the cleansing power of the lower atmosphere at a level that was previously underestimated.

By applying chemical physics techniques to ozone dissociation, we have not only unraveled an atmospheric problem but have learned more details about the nature of the photodissociation process. Quantitative separation of spin-allowed and spin-forbidden processes has been possible, and the role of internally excited species in controlling the reaction dynamics has been measured directly. One needs to remember these lessons for future studies in atmospheric chemistry. There are many other species whose weak absorptions in the visible or near-ultraviolet determine their roles in the atmosphere, and we could expect similar wavelength- and temperature-dependent dissociation pathways to be significant. We give as potential possibilities the photolysis of chlorine and bromine nitrates, the NO_3 radical, and formaldehyde. Atmospheric chemists and chemical physicists still have a lot to learn from each other.

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