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Red sky at night: Long-wavelength photochemistry in the atmosphere

D.J. DONALDSON*
University of Toronto, Canada

CHRISTIAN GEORGE
Université De Lyon, France and Institut De Recherches Sur La Catalyse Et L’Environnement De Lyon, Villeurbanne, France

VERONICA VAIDA
University of Colorado, Boulder, Colorado

Chemical reactions occurring in the atmosphere exert a key influence on air quality at the local and regional scales. On a global scale they have a strong affect on climate, through formation and removal of greenhouse gases, as well as driving cloud formation. Earth’s atmosphere is composed roughly 99% of two gases: molecular nitrogen (N₂; ~ 78%) and molecular oxygen (O₂; ~ 21%), with variable and highly local amounts of water vapor (H₂O; up to a few percent), as well as various trace gas species (such as CO₂, presently at a concentration of a little less than 0.04%). On Earth, “atmospheric chemistry” involves chemical species present only in trace amounts, and is almost exclusively oxidative. Because O₂ is not particularly reactive toward closed shell compounds (those without free electrons), chemistry is initiated by the formation of reactive free radicals, which are then oxidized via the addition of molecular oxygen. Since this addition reaction itself generates free radicals, it is but one such reaction in a sequence, which together comprise an oxidizing chain reaction system in the atmosphere. There is a multitude of organic species in the atmosphere, the most abundant of which is methane (CH₄), which are all eventually oxidized to CO₂ and H₂O, either by gas or aerosol phase processes.

Ultimately, free radicals in the atmosphere are all generated photochemically with short wavelength radiation. This can be a direct process, such as that shown for formaldehyde in reactions R1–R3 below, or indirect, such as the formation of OH through reaction of electronically excited O atoms which efficiently react with H₂O and organic molecules, as illustrated in reactions R4 and R5.

\[
\begin{align*}
\text{HCHO} + h\nu & \rightarrow \text{H} + \text{HCO} \quad \text{(R1)} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \quad \text{(R2)} \\
\text{HCO} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CO} \quad \text{(R3)} \\
\text{O}_2 + h\nu (\lambda < 305 \text{ nm}) & \rightarrow \text{O}^3\text{D} + \text{O}_2 \quad \text{(R4)} \\
\text{O}^3\text{D} + \text{H}_2\text{O} & \rightarrow 2\text{OH} \quad \text{(R5)}
\end{align*}
\]

In the presence of high levels of NOₓ (= NO + NO₂) the HO₂ radicals formed in reactions such as R2 and R3 are rapidly converted to the hydroxyl radical (OH•), which is very reactive toward most organic and many inorganic compounds; these reactions of OH are the primary formation mechanism for radicals in the atmosphere. Similar pathways will also exist in the atmospheric condensed phase (aerosols and clouds) where multiple reactions initiated by UV light will produce radicals or radical anions, and lead to the degradation of both organic and inorganic compounds (as highlighted by the formation of acid rain).

Hydroxyl radicals, despite their low (10⁶ to 10⁷ molecules cm⁻³) daytime atmospheric concentrations, are the most important reactive species in the atmosphere, controlling the concentration of pollutants and greenhouse gases. Understanding what controls the abundance of these radicals is paramount for accurately modeling the atmosphere’s oxidizing capacity and to predict future change. Accordingly, over the decades since Hiram Levy (1) highlighted the central role played by OH radicals in the troposphere, great attention has been given to understanding their chemistry, which is now fully described in textbooks of environmental and atmospheric chemistry (2).

Quite recently, with advances in gas-phase measurement techniques, it has become possible to directly monitor the OH concentration in the troposphere along with several other reactive radical species (such as HO₂, RO₂, NO₃, etc.) (3, 4). Taking advantage of these developments, several field campaigns have highlighted unpredicted levels of OH over the pristine Amazon forest (5) and in the Pearl River Delta, China (6). These studies point to unknown OH sources and/or previously unknown chemical processes, suggesting missing sources or cycling of radicals, and requiring new
ideas and approaches which go beyond textbook knowledge—
from the UV to the visible and beyond!

For this reason, understanding all possible initiation
reactions, such as R1 and R4, is still of fundamental
importance to our ability to predict and model atmospheric
chemical processes. These photochemical reactions are
analyzed as first-order kinetic processes, with a photochem-
cal rate coefficient, \( J \), which depends upon the absorption
coefficient \( \sigma(\lambda) \) of the absorbing compound, the quantum
yield for the dissociation \( \phi(\lambda) \), and the available photon flux
\( I(\lambda) \):

\[
J = \int \sigma(\lambda) \phi(\lambda) I(\lambda) d\lambda.
\]

This expression encapsulates the principle that, in order
to dissociate, a compound must absorb available radiation
in a wavelength region in which this photochemistry can
and will occur. Because typical chemical bond energies are
in the 100s kJ mol\(^{-1}\) range, the conventional picture requires
ultraviolet solar radiation to effect bond-cleaving photo-
chemistry, such as illustrated in R1 and R4, in the atmosphere.

Absorption of UV solar radiation by \( \mathrm{O}_3 \) in the upper
atmosphere, and by \( \mathrm{O}_3 \) in the upper-mid stratosphere, gives
an altitude and solar zenith angle dependence to the
wavelengths of light available in the atmosphere. The longer
pathways associated with higher altitudes and larger zenith
angles (i.e., as the sun approaches the horizon) mean that
shorter wavelengths are attenuated for these situations. This
fact gives rise to photochemistry which depends on altitude,
season, and time of day. At the lowest altitudes, essentially
all of the higher energy UV radiation is attenuated, leaving
light of \( \lambda > 290 \text{ nm} \) to effect any photochemistry. Light in the
visible and longer wavelength regions (\( \lambda > 400 \text{ nm} \)) is very
much more abundant than higher energy radiation (in the
UV region) at all altitudes and solar zenith angles. Although
visible radiation may be sufficiently energetic to rupture
weaker chemical bonds, it is generally not in the correct
wavelength range to excite electronic transitions of atmo-
spherically relevant molecules. Therefore, light in this spectral
region is not usually considered as a driving force in
atmospheric chemistry.

However, in the mid-1990s, in response to model predic-
tions which disagreed with measured stratospheric \( \mathrm{HO}_3 \),
especially at high solar zenith angle (7), two of the present
authors suggested that overtone-mediated photodissociation
of \( \mathrm{HO}_3 \)-containing species by red light (i.e., in the visible
and near-IR regions) could be important (8). Inclusion of the
additional \( \mathrm{HO}_3 \) produced by this novel (to atmospheric
chemists) form of photochemistry reproduced the “red sky”
temporal profiles of the observations and went some way
toward resolving the discrepancies between modeled and
measured \( \mathrm{HO}_3 \) (4, 8–12). In the following, we discuss some
recent work which further explores this mechanism, as well
as introducing a second, hitherto little-considered atmo-
spheric mechanism: radical formation via photosensitized
reactions. With examples of reactions driven by these
mechanisms, we show that long wavelength solar radiation
may play an important role in atmospheric chemistry,
especially in the production of oxidants.

**Overtone-driven Chemistry**

As indicated above, one way in which long wavelength
radiation may promote atmospheric radical formation is
through absorption by a gas-phase molecule into high-lying
vibrational levels. If these levels contain sufficient energy to
induce reaction, radicals may be formed (13, 14). The reaction
may either be a unimolecular dissociation of the initially
excited molecule, or a bimolecular reaction with another
species which is rendered energetically favorable via excita-
tion by red light.

In polyatomic molecules containing \( \mathrm{O} - \mathrm{H}, \mathrm{C} - \mathrm{H}, \) and \( \mathrm{N} - \mathrm{H} \)
groups, the small mass of the hydrogen atom means that
\( \mathrm{X} - \mathrm{H} \) stretching frequencies are considerably higher than
those of other vibrational modes. This feature and the
generally large anharmonicities associated with such \( \mathrm{X} - \mathrm{H} \)
states, give rise to absorption transitions to higher
vibrational levels becoming less “forbidden” (and hence
stronger) than for other types of overtone absorption. At
higher vibrational levels these transitions become sufficiently
separated from the rest of the molecular vibrations to be
treated by the “local mode” approximation, in which each
\( \mathrm{X} - \mathrm{H} \) vibration is taken to be an independent anharmonic
oscillator (15). Spectroscopically, the latter conditions
that overtone absorptions are well separated from other
absorptions; Figure 1 illustrates this for nitric acid (\( \mathrm{HNO}_3 \)),
where the transitions to \( v = 3 \) and \( v = 4 \) of the OH stretch
are shown (16).

As shown in this figure, vibrational overtone transitions
to states with 3–6 quanta of OH stretch occur in the near-IR
(NIR) to visible region of the spectrum. The absorption
intensities for such \( \Delta v = n \) transitions are much smaller than
those to electronic states, and decrease, typically by an order
of magnitude, with increasing \( n \). These levels are sufficiently
energetic to cause cleavage of weak bonds in several
atmospherically important molecules, such as \( \mathrm{HNO}_3 \), \( \mathrm{HONO}_2 \), \( \mathrm{HO}_3 \), \( \mathrm{NO}_3 \), which may then cause their dissociation
to \( \mathrm{HO}_3 + \mathrm{NO}_3 \) (11, 12, 14, 17, 18). This process is indicated
in Figure 1 for \( \mathrm{HO}_3 \), where the initial excitation in OH
stretching motion, at energies above the dissociation limit
to \( \mathrm{OH} + \mathrm{NO}_3 \), may be transformed to motion along the \( \mathrm{N} - \mathrm{O} \)
dissociation coordinate. In the case of peroxynitric acid
(\( \mathrm{HO}_3 \mathrm{O}_2 \)) the dissociation limit is reached at the \( v = 3 \) level
of the OH stretch, with thermally assisted dissociation
possible from the \( v = 2 \) level as well (12). Overtone-initiated
dissociation of this molecule from OH vibrational levels \( v \geq 2 \)
has been shown to be an important source for \( \mathrm{HO}_3 \) in the
free troposphere (9) and lower stratosphere (4, 10, 19),
resolving a major discrepancy between measurements
and models.

Recent laboratory studies have responded to suggestions
based on theoretical modeling that red-light initiated chem-
istry is possible in many other acids and alcohols whose
excited states lie far in the UV region of the spectrum, outside
the atmospheric window. In addition to direct bond cleavage,
molecules with a high degree of internal excitation may
undergo rearrangements, followed by dissociation to mo-
lcuar products. For example, sulfuric acid (\( \mathrm{H}_2\mathrm{SO}_4 \)) has been
predicted to undergo a unimolecular dehydration reaction
to form \( \mathrm{SO}_3 \) and \( \mathrm{H}_2\mathrm{O} \) following excitation to \( v \geq 4 \) of an OH
stretching vibration—corresponding to energies well below
the weakest individual bond in the acid (20–22).

Overtone pumping has also been predicted to lead to HF
elimination from trifluoroacetic acid (\( \text{CF}_3\text{COOH) (23) and perfluoroalcohols (24), and}
and decarboxylation of malonic (\( \text{CH}_2\text{(COOH)}_2 \)) (25) and pyruvic (\( \text{CH}_3\text{COCOOH) (26 acids.}
Recent laboratory studies and “on the fly” dynamical simulations have investigated the long wavelength photo-
chemistry of pyruvic (26, 27) and glyoxylide (\( \text{HCOCOHH})
(28, 29) acids, and shown that overtone-driven decarboxy-
lation is both rapid and efficient. In both of these examples,
photoreaction occurs in less than 10–12 seconds—much more
rapidly than collisional deactivation—and generates highly
reactive carbene radicals in addition to the \( \mathrm{CO}_2 \) product.
Such hydrocarbon radical-generating processes will give rise
both to increased \( \mathrm{HO}_3 \) production and to new aerosol particle
formation, via condensation of the oxidized products. This
will be important if the lifetimes against long wavelength
photochemistry are similar to or shorter than the time for

\[ J = \int \sigma(\lambda) \phi(\lambda) I(\lambda) d\lambda \]
scavenging by \( \text{H}_2\text{O} \) droplets or aerosol particles. This limit may be achieved for reactions having barriers such that excitation into the \( v = 3 \) (or lower) level of an \( \text{OH} \) stretch will activate the chemistry.

An interesting wrinkle to the above takes place in the presence of \( \text{H}_2\text{O}(g) \): by forming hydrogen-bonded complexes with acids and alcohols, \( \text{H}_2\text{O} \) can act as a catalyst to many of the elimination reactions \((24, 25, 30, 31)\), lowering the barriers by providing a "hydrogen shuttle" \((31)\). The lower barrier may allow excitation of lower \( \text{OH} \) vibrational levels, which absorb more strongly, to activate the chemistry. Calculated equilibrium constants for such complexes in the troposphere indicate a wide range of possible concentrations, with fractions of the acid or alcohol sequestered in a \( \text{H}_2\text{O} \) complex from \( \sim 10^{-4} \) to 0.1 \((22, 24, 25, 30)\). Combining the increase in the photochemical rate (due to lower vibrational levels becoming important) with the calculated fraction of complexes suggests that this catalyzed chemistry may be as important or more important than the uncatalyzed process. The result, which has not yet been tested experimentally, is that under these conditions, the environmental fates of compounds such as perfluoroalcohols, \( \alpha \)-hydroxy acids, and organic diacids may be governed by overtone photochemistry.

**Photocatalyzed Processes**

Another manner in which longer wavelength radiation may induce chemical reaction is through a photosensitized process, in which compound \( A \), associated with a surface exposed to the atmosphere, absorbs long wavelength light and subsequently transfers sufficient energy to compound \( B \), which does not absorb such light, thus causing a chemical transformation. For example, in natural waters, dissolved organic matter (DOM) absorbs visible and near-UV radiation and transfers energy to dissolved \( \text{O}_2 \), forming "singlet oxygen", which reacts with the DOM to yield \( \text{OH} \cdot \) \((32)\). Thus \( \text{O}_2 \), which does not absorb actinic radiation, may be activated indirectly. Another example is visible light absorption by particles of \( \text{TiO}_2 \), which creates negative electrons and positive "holes" near that semiconductor’s surface. The availability of these highly reactive species gives rise to heterogeneous redox reactions, notably the production of \( \text{OH} \) from water molecules present at the \( \text{TiO}_2 \) surface.

Similar redox chemistry is initiated by biogenic compounds exposed to the atmosphere, in aerosol particles, or at sea and lake surfaces. Chlorophyll is a strongly photoactive compound: it absorbs light throughout the visible part of the solar spectrum and thus makes electrons available to
participate in reduction reactions. When present at salt water surfaces, chlorophyll which is photexcited (even just with red light) oxidizes halide anions, forming halogen atoms (33, 34). Some of these may react with the chlorophyll and other organic compounds present at the water surfaces and forming gas, leading to the release of lighter organics from such surfaces, forming gas-phase radicals; others are released into the gas phase directly in atomic or molecular form. But chlorophyll is only one example, as the same photoredox chemistry is observed using benzophenone as the absorbing species (35). This implies that halogen and radical release from seawater may be quite general, as ocean surfaces are known to be coated with a thin layer of biogenic material (the "marine microlayer"), which contains myriad photoreactive compounds (36, 37). Indeed, recent measurements have indicated the presence of reactive halogen species in the marine boundary layer (38–40).

One method by which atmospheric aerosols affect climate change is via warming by visible light absorption by the particle. The electronic absorption transitions which are responsible for exciting the particle surfaces may then also allow photoreduction, by supplying electrons in the same manner as chlorophyll. For example, on illuminated mineral dust, humic, and soot surfaces, NO\(_2\) undergoes heterogeneous reduction to HONO, with over 50% efficiency—and in the case of humic acids, an efficiency approaching 100% (41–43). HONO is an important source for OH in the atmosphere, as it is rapidly photolyzed by near-UV radiation, at wavelengths longer than required for reactions R1 and R4. Thus, the photoreduction of NO\(_2\) gives a long wavelength source for OH, while perturbing only a little (due to the relative importance of R7 vs R8) the photostationary state relationship between NO\(_2\) and O\(_3\):

\[
\begin{align*}
\text{NO} + \text{O}_3 & \rightarrow \text{NO}_2 + \text{O}_2 \quad (R6) \\
\text{NO}_2 + \text{O}_2 + \text{hv} & \rightarrow \text{NO} + \text{O}_3 \quad (R7) \\
\text{NO}_2 + \text{hv}(\text{heterogenous}) & \rightarrow \text{O}_3 \quad (R8) \\
\text{HONO} + \text{hv}(\lambda < 390 \text{ nm}) & \rightarrow \text{OH} + \text{NO} \quad (R9)
\end{align*}
\]

This chemistry does not occur in the dark to any appreciable extent, but is induced via absorption of actinic radiation by the solid substrate. Although a recent report suggests that electronically excited NO\(_2\) may react efficiently to form HONO in the gas phase (44, 45), this finding is the subject of considerable debate (46, 47). For the heterogeneous process on all three substrates listed above, the photoreduction persists over several hours without loss of efficiency. This implies that the substrate itself is not being depleted through supplying the H during the reduction R8, but that there exists another source of H atoms. In the atmosphere this is most probably adsorbed water, which is present ubiquitously on surfaces in the real atmosphere.

A semiquantitative estimate of the importance of such photosensitized chemistry can be estimated from the results of Stemmler et al. (43) who studied the photoenhanced deposition of NO\(_2\) on humic acid and soil surfaces. In the presence of 16.5 ppb NO\(_2\) they observed a photoinduced HONO flux of 2.5 × 10\(^{10}\) molecules cm\(^{-2}\) s\(^{-1}\) under UV-A irradiation and 1 × 10\(^{10}\) molecules cm\(^{-2}\) s\(^{-1}\) in the visible region. Using these results, and scaling for the lamp intensities, the total photochemical HONO production may be estimated to be ∼5 × 10\(^{10}\) molecules cm\(^{-2}\) s\(^{-1}\) for a moderately polluted atmosphere (∼20 ppb NO\(_2\), which is an abundance typically reached daily in urban centers) and typical midday solar irradiances (300–700 nm) ∼400 Wm\(^{-2}\). Since such surfaces are ubiquitous in the environment, this process can lead to high daytime concentrations of HONO; the flux estimates above predict that such processes could account for up to 60% of the integrated OH radical source strength, overwhelming reactions R1 to R5 in importance and suggesting that this chemistry may be observed in field measurements. These ideas are captured in Figure 2, which illustrates how surface photochemistry influences OH production in urban settings.

Mineral dust surfaces are also important substrates for photosensitized chemistry. Every year between 1000 and 3000 Tg of mineral aerosol is emitted globally and injected into the atmosphere. Ndour et al. (42) demonstrated that these surfaces are photochemically active under atmospherically relevant conditions, giving rise to a large photoenhanced uptake of NO\(_2\). Simulations with the LMDz-INCA model indicated that such mineral dust photochemistry may reduce the NO\(_2\) level up to 37% during a dust event in the free troposphere, causing a change in the O\(_3\) concentration of 5% (42). When averaged over the globe, the decrease in simulated NO\(_2\) concentrations in the free troposphere amounts to 3.0%.

**Outlook: Reevaluating Atmospheric Cleansers!**

Could long wavelength photochemistry help clean the atmosphere? The examples discussed above suggest that this could well be! By enhancing the production of HO\(_x\) radicals which initiate the degradation reactions of atmospheric pollutants, these photochemical mechanisms could have a significant impact on atmospheric processes. Assessing the
full extent to which they influence the atmosphere will certainly require further research. We need to know how general surface photochemistry processes are. They may indeed affect a variety of deposition processes, which are mostly seen as being sinks for atmospheric trace compounds. If these supposed sinks are in fact photochemically driven processes, there may be an enhanced interplay between gaseous components and condensed matter (i.e., at ground or airborne particles) as highlighted by the example of NO

In the atmosphere, all photochemical reactions occur against a “clock” set by collisional deactivation of the excited species generated by absorbing light. If a reaction is too slow, the rate of energy flow and reaction, vs energy loss by collisions. At high solar zenith angles by overtone-induced dissociation of CN layers.

James Donaldson is a Professor of Chemistry at the University of Toronto. Christian George is a senior research scientist at IRCELYON (CNRS and Université de Lyon 1). Veronica Vaida is a Professor of Chemistry and a CIRES Fellow at the University of Colorado. Please address correspondence to jdonalds@chem.utoronto.ca.

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