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Trace gases are responsible for the atmospheric processes underlying air pollution and global change. Analysis of the distribution of stable isotopes in these gases is a way of gaining additional knowledge that may not otherwise be available. This approach requires knowledge of the isotopic signature of emissions sources and chemical reactions. This review focuses on the chemical physics of the processes underlying the distribution of stable isotopes in atmospheric gases.

1 Introduction

Many chemical and physical processes modify the distributions of isotopic species in the atmosphere. Isotopologues are

molecules that differ according to the number of isotopic substitutions, for example CH_4 and CH_3D . Isotopomers differ according to the position of the substitution, for example symmetric and asymmetric ozone, $^{16}\text{O}^{18}\text{O}^{16}\text{O}$ and $^{16}\text{O}^{16}\text{O}^{18}\text{O}$ (constitutional isomers), or (*Z*)- and (*E*)- $\text{CH}_3\text{CH}=\text{CHD}$ (stereoisomers). Analysis of the distribution of stable isotopes in atmospheric trace gases is a way of gaining additional knowledge about a gas that may not otherwise be available. However, specific knowledge regarding the isotopic signature of emissions sources and chemical reactions is needed in order to construct an isotope budget for a given compound. Trace gases obey the mass balance equation, *i.e.* the change in the mass of a compound in the atmosphere over time must be equal to the imbalance between production and loss. There are a number of atmospheric phenomena that have been illuminated by the study of the distribution of stable isotopes, including air

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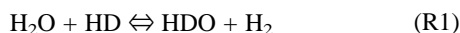


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pollution, global warming, ozone depletion and the history of Earth's climate. This review will focus on the chemical physics of the processes underlying the distribution of stable isotopes in atmospheric gases.

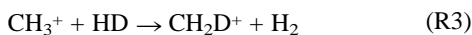
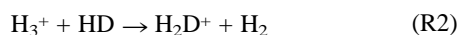
Atomic nuclei consist of protons and neutrons. The number of positively charged protons in the nucleus determines the atomic number Z , and the sum of protons and neutrons determines the mass number A . The atomic number determines the position of a nuclide in the periodic table. The mass number is given as a left superscript of the elemental symbol, *e.g.* ^{14}C , 'carbon-14.' The most basic example of isotopic enrichment in the Earth's atmosphere is provided by the isotopes of the element hydrogen, protium and deuterium. Deuterium was discovered by Urey, Brickwedde and Murphey in 1932. Urey proceeded to develop the theory of isotopic fractionation that is a cornerstone of isotope geophysics. ^1H and ^2H (or less formally, H and D) were formed by nucleosynthetic reactions in the first few hot and dense minutes of the Universe following the Big Bang. Relatively uniform D/H ratios of *ca.* 10^{-5} are found throughout the interstellar medium, and on Jupiter and Saturn, the gas giants. On Earth the main reservoir of hydrogen is the ocean, and the D/H ratio is $1.5576 \pm 0.0005 \times 10^{-4}$ for Standard Mean Ocean Water (SMOW). The Earth was formed by the accretion of chunks of ice and dust in the solar nebula. Most of this original water is now in the oceans. The D/H ratio in remnants of the terrestrial planet-forming material still found in our solar system, such as meteorites and Comet Halley, is close to that of SMOW.¹

The question is why ocean water, derived from the ices in the solar nebula, is enriched in D by an order of magnitude relative to the Universe. A number of physical mechanisms may be involved, such as the rate of escape of heavy and light isotopologues from a planetary atmosphere (Section 2). But the enrichment is impossible to explain without an underlying chemical mechanism. First, we should consider isotope exchange reactions of the type:



At low temperature, equilibrium favors the right hand side, and water becomes enriched in deuterium relative to molecular hydrogen. Similar equilibria govern the partitioning of D/H in methane and ammonia. It is a general feature of equilibrium isotope effects (Section 3) that the heavy isotope becomes enriched in the more tightly bound species. It is necessary to consider not just the position of chemical equilibrium, but also the rate of reaction (Section 4).

Because of the activation barrier of the forward and backward reactions in (R1), equilibrium may not have been established within the lifetime of the solar nebula. The observed enrichment could also be due to barrierless ion exchange reactions,



known to be important in interstellar molecular clouds. Reactions (R2) and (R3) are exothermic by 1.9 and 3.1 kJ mol^{-1} respectively. As we will see below, reactions (R1)–(R3) are driven by differences in the zero point vibrational energy of the reagents and products. There is an interesting and detailed

discussion of D and H fractionation in planetary atmospheres in the monograph by Yung and DeMore.¹

With the exception of hydrogen and helium, the interaction between Earth and space has involved negligible amounts of material compared to what is present in the Earth itself. The elemental composition of the planet, with the exception of transformations related to nuclear decay, is fixed. However the partitioning of the elements and their isotopes within the biogeochemical earth system continues to evolve. Many of these processes, especially those relevant to geological isotope distributions, involve phase equilibria and are discussed in Section 3.

The Earth's atmosphere however is far from chemical equilibrium. It resembles a low temperature flame in which solar radiation initiates chains of radical reactions. The rates of chemical reaction, considered in Section 4, vary considerably with isotopic substitution. The physical processes resulting in isotopic enrichment are made to appear pedestrian by the wide spectrum of behaviors shown by the chemical effects. As detailed in Section 4, the rate of $^{16}\text{O} + ^{18}\text{O}_2 + \text{M} \rightarrow ^{16}\text{O}^{18}\text{O}_2 + \text{M}$ is more than 50% faster than the rate of $^{18}\text{O} + ^{16}\text{O}_2 + \text{M} \rightarrow ^{18}\text{O}^{16}\text{O}_2 + \text{M}$.² In addition to powering photosynthesis, the sun has a direct effect on the atmosphere through photolysis and photochemistry, the subject of Section 5. Human activities such as agriculture and industry also affect the composition of the atmosphere; the isotopic signature of emissions sources are considered in Section 6. This Section also describes how all of this information can be combined to produce an isotope budget. Knowledge of the isotopic fingerprint of a given process can be used to measure highly reactive transient species by proxy, to identify or exclude specific reactions in the atmosphere, and to constrain the sources and sinks of greenhouse gases such as nitrous oxide, methane and carbon dioxide.

2 Physical mechanisms

At the beginning of the twentieth century, some curious features of the elements of Mendeleev's periodic table had been noted. To begin with, atomic mass did not always increase with atomic number. For example, K is lighter than Ar, even though it has a larger atomic number. Other workers showed that lead samples from different sources have different atomic weights, and that different samples of thorium salts had different rates of decay. In 1914 Frederick Soddy proposed that a single element of the periodic table could comprise several isotopes. Thomson modified his cathode ray tube to measure the charge to mass ratio of heavier species. By 1919 the 'mass spectrograph' had identified 212 of the 287 naturally occurring nuclides.³ This Section will consider the physical mechanisms that can lead to the separation of nuclides in the atmosphere. Isotopic abundances relevant for studies of atmospheric trace gases are found in Table 1.

2.1 The kinetic theory of gases

The kinetic theory of gases assumes that the total energy of a gas is determined only by the kinetic energy of the gas particles. To

Table 1 Fractional abundance of some isotopes found in atmospheric trace gases (CRC Handbook, 79th ed.)

Hydrogen	^1H	0.999844	D(^2H)	0.000156	T(^3H)	Small	
Neon	^{20}Ne	0.9051	^{21}Ne	0.0021	^{22}Ne	0.0922	
Carbon	^{12}C	0.9890	^{13}C	0.0110	^{14}C	Small	
Nitrogen	^{14}N	0.9964	^{15}N	0.0036			
Oxygen	^{16}O	0.99763	^{17}O	0.000375	^{18}O	0.001995	
Sulfur	^{32}S	0.9502	^{33}S	0.0075	^{34}S	0.0421	^{36}S 0.0002
Chlorine	^{35}Cl	0.7577	^{37}Cl	0.2423			
Argon	^{36}Ar	0.00337	^{38}Ar	0.0063	^{40}Ar	0.9960	
Bromine	^{79}Br	0.5069	^{81}Br	0.4931			

a good approximation, the behavior of atmospheric gases is 'ideal,' in that the kinetic theory of gases pertains. According to the equipartition theorem, gas phase isotopic analogues in thermal equilibrium have the same kinetic energy (E_k) in each degree of freedom:

$$E_k = k_B T/2 = mv^2/2 \quad (1)$$

Where k_B is Boltzmann's constant, T temperature, m mass and v velocity. Two species with different mass in thermal equilibrium will have the same average kinetic energy, and unique velocities. The ratio of the velocities is given by the square root of the inverse of the ratio of the masses. According to the kinetic theory of gases, the mean speed of a particle is given by:

$$c = (8k_B T/\pi m)^{1/2} \quad (2)$$

The rate of a gas phase chemical reaction can be considered as the rate of collision between the reagents times the probability that a given collision will result in reaction. It follows from the two previous equations that light species undergo collisions more frequently. The collision rate is given by:

$$z = 2^{1/2} \sigma c p / (k_B T) \quad (3)$$

Here σ is the collision cross section and p pressure. Thus if two isotopic species have the same probability of reaction upon collision, the ratio of their reaction rates is simply the square root of the inverse of the ratio of their masses.

2.2 Jeans escape

In 1916 Sir James Jeans, a pioneer of atmospheric chemistry, developed a theory to explain the absence of an atmosphere on the moon. The escape of a molecule into space depends on the ratio of the gravitational binding energy of the molecule (GMm/r_c) to its thermal kinetic energy $k_B T_c$:

$$\lambda = \frac{GMm}{k_B T_c r_c} \quad (4)$$

Here G is the gravitational constant, M the mass of the planet, m the mass of the molecule, T_c the temperature at the critical level from which escape occurs and r_c the distance from this level to the center of the planet. The flux of molecules from the atmosphere into space ($\text{cm}^{-2} \text{s}^{-1}$) is then given by:

$$F = n_c \frac{v}{2\sqrt{\pi}} (1 + \lambda) e^{-\lambda} \quad (5)$$

Where, n_c is the number density (cm^{-3}) of the species at the critical level, and $v = (2k_B T/m)^{1/2}$ is the most probable speed of a Maxwell distribution of molecules at T_c . Jeans showed that the moon is not sufficiently massive to retain an atmosphere. In contrast Jupiter and Saturn are so massive that $k_B T$ is small compared to the gravitational binding energy, and atmospheric escape is not important.

The terrestrial planets Venus, Earth and Mars are intermediate cases, where some atmospheric evolution due to Jeans escape has occurred. The D to H ratio on Mars is five times higher than on earth. Since the mass of the planet is smaller, much more material has escaped from the Martian atmosphere into space. If we assume the hydrogen is present as water distributed equally over the surface of the planet, and taking a uniform escape rate over time, the observed ratio implies that Mars originally had about 3.6 m of water, about 20 cm of which is left today.¹

2.3 Rayleigh distillation

In general, we may consider a fractionation process with rates k and k' for the removal of isotopic species with concentrations

[X] and [X']. For a kinetic process the enrichment factor $\epsilon = \alpha - 1$, characteristic of a given process, will depend on $\alpha = k/k'$, the fractionation factor or relative rate. By convention α is taken as the reaction rate of the light species (X) divided by the rate for the heavy species (X'). Note that it is not uncommon to define the fractionation factor as the ratio of the reaction rate of the rare to the common isotopologue, often in conflict with the light over heavy definition. We use here the definition accepted by IUPAC, light over heavy.

The 'isotope ratio' or mole fraction R of an isotopic species is the concentration of the isotopically heavy species divided by the concentration of the light species in a given sample. The isotope ratio of the remaining species is governed by the Rayleigh distillation formula,

$$R = R_0 f^\epsilon \quad (6)$$

where f is the fraction of the original quantity of isotopically light sample remaining. If ϵ is positive the heavy isotope will become depleted in the remaining sample.

For an equilibrium process we may define the fractionation factor $\alpha = R/R'$, for example R could be the D/H ratio in ice and R' the ratio in water vapor. The Rayleigh distillation formula still pertains.

In isotope ratio mass spectroscopy the difference in the isotope ratio between two substances can be determined with great accuracy. The 'delta value' is defined as follows:

$$\delta_x = \frac{R_x - R_{\text{std}}}{R_{\text{std}}} \quad (7)$$

Delta is most often given in units of per mil. For sufficiently small enrichments one may use the approximation:

$$\delta \approx \delta_0 + \epsilon \ln(f) \quad (8)$$

(Remembering that ϵ is the enrichment factor and f the fraction of isotopically light sample remaining.) It is important to emphasize that the enrichment factor is independent of the extent of reaction and is characteristic of the transformation process itself, and is thus of great use when discussing reaction mechanisms. On the other hand environmental samples have a certain composition characterized by δ , which will vary depending on ϵ and f .

2.4 Diffusion

At a given gas temperature, the diffusional velocity of a light species is higher than that of a heavy species. Consideration of eqn. (1) allows the derivation of Graham's law of diffusion:

$$v_1/v_2 = (m_2/m_1)^{1/2} \quad (9)$$

In the previous subsection we noted that the gravitational potential energy of a given gas depends only on the molar mass m of the gas. The barometric formula,

$$p(z) = p(0) \exp(-z/H) \quad (10)$$

indicates that each gas should have a unique scale height $H = k_B T/(mg)$ in the atmosphere. In eqn. (10), $p(0)$ is the pressure at the bottom of the atmosphere, and $p(z)$ the pressure at altitude z . The scale height of the Earth's lower atmosphere is ca. 7.4 km; at this altitude the pressure has dropped to $1/e$ of the pressure at the surface. It was once suggested that CFCs would never reach the stratosphere, that because of their high molecular weight relative to atmospheric N_2 and O_2 , and consequent low scale height, they would be concentrated near the surface of the planet. However, CFCs do reach the stratosphere, and further, the composition of the atmosphere is remarkably uniform from the surface to the homopause, about 100 km altitude. The mechanism of the separation of gases according to their individual scale height is diffusion, and below the homopause turbulent mixing is more rapid than diffusional separation.

Above the homopause separation takes place, for example the mixing ratio of O₂ decreases with altitude. For the same reason that CFCs are uniformly mixed in the lower atmosphere, turbulent mixing driven by advection and convection is not a mechanism that produces isotopic fractionation. It can however blur the signatures of other processes, for example by mixing enriched and unreacted gas parcels.

Given a suitable environment, isotopic species will be fractionated by diffusion in the atmosphere. For example, snowfall results in the glaciers that cover Antarctica and Greenland. At a certain depth the snow is changed into ice, trapping bubbles of atmospheric air. This air is enriched in the heavy isotopologues of N₂, O₂ and other gases because of their relatively slower rates of diffusion. As another example, the overall rate of a heterogeneous reaction may depend on the diffusion of a reagent molecule to an aerosol surface, or into the bulk of the condensed phase. In addition, the differing rates of diffusion of water isotopologues in a droplet can lead to concentration gradients when water is evaporating from or condensing on the surface. For an in-depth discussion of isotopic fractionation in liquid/vapor water systems, the reader is referred to the monograph by Criss.³

2.5 Nuclear decay

A thorough discussion of nuclear chemistry is beyond the scope of this review but a few pertinent features can be mentioned. Following the Big Bang, most matter was (and still is) hydrogen, a small fraction deuterium and an even smaller fraction helium. The synthesis of the heavier nuclides in the periodic table occurs inside stars. Nuclei have inherent stabilities, and some general trends are apparent. For example nuclei with even atomic numbers are about ten times more common than those with odd atomic numbers. There is also a preference for mass numbers that are a multiple of four. The four nuclides ¹⁶O, ²⁴Mg, ²⁸Si and ⁵⁶Fe make up 85% of the mass of Earth.³ Unstable nuclides of many of the elements are known, and the fission of these nuclei can be used to study atmospheric processes.

We will give one example.⁴ Soils emit ²²²Rn, a nuclide which decays to ²¹⁰Pb with a half life of 3.8 days. In the atmosphere lead atoms quickly condense onto existing aerosol particles. Analysis of this lead indicates that the particles have an atmospheric lifetime of 8 days, determined by deposition. In the stratosphere and upper troposphere, ⁷Be is formed by the collision of cosmic rays with nitrogen nuclei, and it also condenses onto preexisting aerosol particles. Consideration of the mass balance of ⁷Be indicates that these aerosols are removed from the atmosphere with a lifetime of 24 days. Analysis of these two radioactive isotopes gives an interesting picture of atmospheric aerosol deposition rates. Aerosols near the surface, where humidity and rainfall are greater, are found to have a shorter lifetime.

3 Chemical equilibrium

Equilibrium isotope effects have proven themselves to be of great use in earth system science, forming the basis of isotope geochemistry. The pioneering work of H. C. Urey showed how ¹³C and ¹⁸O enrichments in carbonate shells can be used as a paleothermometer, recording the temperature of the ocean when the shell was formed.³ Subsequent work has examined a large variety of systems.

According to the Born–Oppenheimer approximation, we may separate nuclear and electronic motion. Electrons move fast relative to the massive nuclei, so it is a good approximation to treat them as if they move in a potential determined by fixed nuclei. Accordingly, a change in the mass of the nuclei will not

change the potential energy surface of a system. A change in mass will however change the vibrational frequencies of the system. In Fig. 1 we see that while the potential energy surface

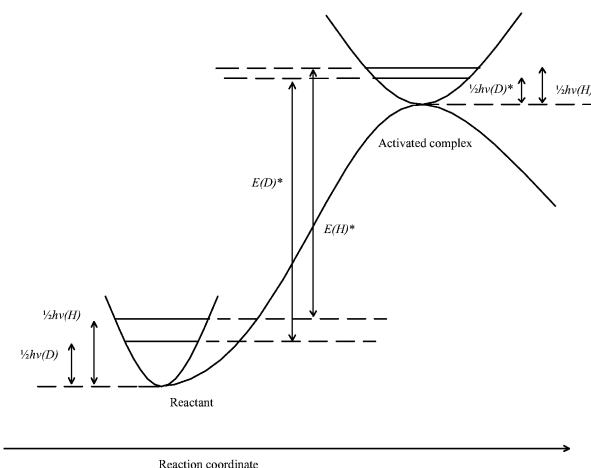


Fig. 1 Diagram of the stretching vibration of RH in an unperturbed state, and upon formation of the activated complex in reaction $RH + X \rightarrow R + HX$. Zero point energies of hydrogen and deuterium substituted molecules are shown as well as the activation energies for reactions involving both compounds.

of a molecule or reaction system may remain invariant to isotopic substitution, the frequencies of the system's normal vibrational modes do change. This in turn affects the zero point energy of the system. As we will see, changes in zero point energy are a central feature of equilibrium isotope effects.

Restating, isotopic substitution does not change the force constant f of a bond, but it does change the vibrational frequency ν . For a harmonic oscillator the frequency of vibration is given by Hooke's Law:

$$\nu = (1/2\pi)(f/\mu)^{1/2} \quad (11)$$

Here μ is the reduced mass of the system. For example the reduced mass of a diatomic AB is given by:

$$\mu_{AB} = m_A m_B / (m_A + m_B) \quad (12)$$

From quantum mechanics we know that even at the absolute zero of temperature, a molecule is still vibrating, and that each normal mode contains half a vibrational quantum of energy. The zero point energy is the sum of the vibrational energy in each mode at zero Kelvin:

$$E_{ZP} = \frac{1}{2} \sum_{i=1}^n \nu_i \quad (13)$$

Here $n = 3N - 5$ for the number of normal modes of a linear molecule, or $3N - 6$ for a nonlinear molecule. N is the number of atoms in the molecule. The zero point energy is unique in that it is a fundamental property of a given molecule. As opposed to translational, vibrational, rotational and on occasion electronic energy states, it cannot be in thermal equilibrium with its surroundings.

Next, consider equilibrium in a system involving the exchange of isotopes X and Y between two chemical reservoirs A and B:



Which has an associated equilibrium constant:

$$K = \frac{[AY][BX]}{[AX][BY]} \quad (14)$$

Statistical thermodynamics tells us that

$$K = \frac{Q_{AY} Q_{BX}}{Q_{AX} Q_{BY}} e^{-\Delta E_0 / kT} \quad (15)$$

where Q is the partition function of a given species, the product of the translational, rotational, vibrational and electronic partition functions. We have taken advantage of the fact that for isotopic exchange reactions, changes in the volume of the system can be ignored. We have not included changes in the internal energy of the reaction as part of the (classical) vibrational partition function. Instead, this is included in the final term of the equation. The term ΔE_0 is the change in the internal energy of the reaction evaluated at 0 K, that is, the change in the zero point energy of the reaction. In many systems, at atmospheric temperatures, the vibrational partition function tends not to change very much with isotopic substitution. Instead the main effect is due to the change in the quantum zero point energy of the reaction. We have written eqn. (15) to emphasize this distinction. The effect of isotopic substitution on equilibrium constants was considered by Bigeleisen and Mayer in 1947.⁵

In the same year, Urey described isotope exchange reactions by considering each molecule relative to the separated atoms. He derived an equation for the ratio of the partition function of a substituted molecule (Q_Y) relative to the unsubstituted one (Q_X):

$$\frac{Q_Y}{Q_X} = \frac{Q_{Y,\text{rot}}}{Q_{X,\text{rot}}} \cdot \prod_{i=1}^n \left\{ \frac{1 - e^{-U_{X,i}}}{1 - e^{-U_{Y,i}}} \cdot \frac{e^{-U_{Y,i}/2}}{e^{-U_{X,i}/2}} \right\} \quad (16)$$

Several terms appear on the right hand side of this equation. Starting from the left, we have the ratio of the rotational partition functions. For a linear molecule this can be approximated as $Q_{\text{rot}} = k_B T / (\sigma h c B)$ where c is the speed of light, B the rotational constant and σ the symmetry number of the species (one for heteronuclear diatomics, two for homonuclear diatomics, three for NH_3 , etc.). The rotational partition function for other types of molecules can easily be found in any number of textbooks. The continued product ranges over the number of vibrational normal modes of the system. The term U is the ratio of vibrational to thermal energy, $U = h\nu/k_B T$. The classical vibrational partition function is $1/(1 - e^{-U})$. Finally, the vibrational zero point energy is contained in the term $e^{-U/2}$.

The partition functions depend on temperature, and so do the equilibrium constants. In fact, the distribution of stable isotopes between different reservoirs at equilibrium is an almost perfect thermometer. This has allowed an accurate reconstruction of the climate history of the earth to be assembled, using for example the $\delta^{18}\text{O}$ of carbonate shells in the ocean, and the $\delta^{18}\text{O}$ of ancient water in the Antarctic and Greenland glaciers. The first example depends on the equilibrium between aqueous and carbonate CO_2 , and the second, on the difference in the chemical potential of H_2O and H_2^{18}O in the liquid and gas phase.

4 Reaction kinetics

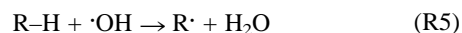
Chemical reaction rates are affected by isotopic substitution. It is helpful to categorize the effects according to the mechanism of the reaction, whether it be *via* abstraction, the formation of an adduct, association, or the assistance of biological enzymes.

4.1 Abstraction

In an abstraction reaction, an atom is taken away from one species by another. When considering the effect of isotopic substitution on the rate of an abstraction reaction, it is reasonable to use the Born–Oppenheimer approximation, in which the electronic and nuclear motions are considered to be separable. Then, isotopic substitution in a chemical reaction or

equilibrium changes the zero point energy of the substituted species but not the potential energy surface of the reaction.

Consider the first step in the oxidation of a typical atmospheric hydrocarbon:



The potential energy of the reaction coordinate for such a reaction is shown in Fig. 1. Transition state theory is a useful theoretical model for the rate of a chemical reaction. In this theory, the rate constant can be obtained from the physical properties of the reactants and the ‘transition state.’ The transition state is the activated complex formed during reaction and from which the products are formed. The object is to calculate the concentration of the activated complex and the rate with which the system goes through the transition state configuration. At the transition state the RH bond is considerably weakened compared to the reagent RH. This reduction in the force constant of the RH bond means that the vibrational frequency is much lower. Now, consider the effect of deuterium substitution on the hydrocarbon. According to eqn. (11), the R–D stretching frequency is $1/(2^{1/2})$ of the R–H frequency. As shown in Fig. 1, while the potential energy surface of the reaction is the same, the activation energy for deuterium abstraction is larger than that for hydrogen abstraction.

To illustrate, consider a typical C–H stretching frequency of 3000 cm^{-1} . The change in the activation energy for D abstraction will depend on the change in the vibrational zero point energy of the bond. Since this bond is weakened in the transition state, we will assume that the change in the zero point energy upon deuterium substitution is zero (a lower limit to the true change). In all the apparent change in the activation energy could be as large as $(\frac{1}{2} \times 3000) - (\frac{1}{2} \times 3000/2^{1/2}) = 440 \text{ cm}^{-1} = 5 \text{ kJ mol}^{-1}$. The resulting decrease in reaction rate for deuterated compounds is known as a primary kinetic isotope effect, primary because the substituted atom is adjoining the bond being broken or formed in the reaction.⁶

Nielsen and coworkers have measured the rate of reaction of a series of isotopically labeled aldehydes.⁷ The properties of the transition state were calculated using *ab initio* techniques. From generalized transition state theory, the rate of reaction is given by:

$$k(T) = \frac{k_B T}{h} \frac{Q^{\text{TS}}(T)}{Q^{\text{R}}(T)} \exp\left(-\frac{(E_{\text{elec}}^{\text{TS}} - E_{\text{elec}}^{\text{R}}) + (E_0^{\text{TS}} - E_0^{\text{R}})}{k_B T}\right) \quad (17)$$

Where the superscript ‘TS’ refers to the transition state and ‘R’ to the reagent. E_{elec} is the electronic energy, and E_0 the vibrational zero point energy. The fractionation factor (*cf.* Section 2.3) is then given by:

$$\alpha(T) = \frac{k(T)}{k'(T)} = \frac{Q^{\text{TS}}(T) \cdot Q^{\text{R}}(T)}{Q^{\text{R}}(T) \cdot Q^{\text{TS}}(T)} \exp\left(-\frac{(E_0^{\text{TS}} - E_0^{\text{R}}) - (E_0^{\text{TS}} - E_0^{\text{R}})}{k_B T}\right) \quad (18)$$

A clear parallel exists between these equations and those appearing in Section 3, namely the contribution of vibrational zero point energy to the isotope effect. It is interesting to note that from a theoretical standpoint, these isotope effects are far from being well-understood. For example, for aldehydic hydrogen abstraction by Cl from CH_3CHO and CH_3CDO at 298 K, $\alpha_{\text{theo}} = 1.639$, whereas $\alpha_{\text{expt}} = 1.343 \pm 0.023$. Even more strikingly, for the Cl reaction rate of CH_2O and CD_2O , using eqn. (18) $\alpha_{\text{theo}} = 2.50$, while $\alpha_{\text{expt}} = 1.302 \pm 0.014$. The discrepancy may be due to the formation of a weak adduct between the atom and the aldehydic oxygen.⁷

An additional consideration should be made when considering the rate of a chemical reaction. Quantum mechanical particle-wave duality introduces wavelike behavior, especially

as mass decreases. The proton is the lightest nucleus, and possesses the greatest quantum wave-like character of any nuclide. One feature of quantum mechanics is that a wavefunction can tunnel through a potential barrier that it would not classically be allowed to cross. Thus, the phenomenon of tunneling through the reaction barrier accelerates a reaction involving the proton, relative to the analogous deuterium reaction. Examples include hydrogen abstraction reactions, and the $\text{CO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}$ reaction discussed in Section 4.2 (see ref. 26).

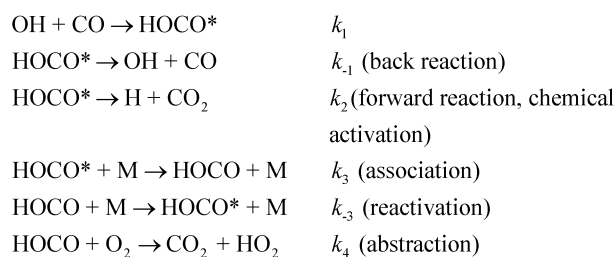
Methane is the most important atmospheric hydrocarbon, and it is removed from the atmosphere by abstraction reactions. The OH radical is the most important reaction partner, and Cl can also play an important role, especially in the stratosphere.⁸ The ^{13}C and D isotope effects have been characterized in the laboratory. These reactions have also been examined using variational transition state theory, however the agreement with experiment is not satisfactory.

The standard kinetic isotope effect considers that the activation energy of a reaction includes a contribution from the internal zero point energies of the molecules. However, some reactions that have no apparent reaction barrier exhibit isotope effects, for example the reactions of OH with H_2O_2 , D_2O_2 and CO. These adduct-forming reactions are discussed in the Section 4.2. Taatjes and Klippenstein have used variational transition state theory to model kinetic isotope effects in barrierless recombination reactions.⁹

4.2 Reactions forming adducts and unimolecular dissociation

Some seemingly simple reactions, in particular those with long lived reaction intermediates, display isotope effects that cannot be explained using the ideas presented in the previous subsection. Adduct forming reactions are characterized by small or negative activation energies and curved Arrhenius plots. As noted by Mozurkewich and Benson, the activated complex is often more likely to fall apart into reagents than products.¹⁰ The process can be described as a competition between two unimolecular dissociation pathways, one forward giving products, and one backwards in which the adduct dissociates into reagents.

To illustrate, consider the atmospheric oxidation of carbon monoxide, the prototypical adduct-forming reaction. The reaction $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ removes 90% of atmospheric CO, 70% of OH, and generates 1/6 of atmospheric CO_2 . The reagents form an adduct, the carboxyl radical. There is a competition between vibrational quenching and two unimolecular pathways, one to form products and one reagents:



RRKM (or ‘unimolecular’) dissociation theory gives us a way of predicting the lifetime of a system with enough internal energy to dissociate. It can be described as microcanonical transition state theory, as it considers the statistical probability that the system will find itself in the critical configuration that divides the adduct from the exit channel.

The RRKM rate constant is given by $k(E) = N(E_t)/h\rho(E_t)$.⁶ Here $N(E_t)$ denotes the sum of states for the active degrees of freedom in the transition state and $\rho(E_t)$ is the density of states for the active degrees of freedom in the reactant. E_t is the sum

of the vibrational and translational (along the reaction coordinate) energy of the transition state and E_v is the total energy minus the rotational energy. If we consider the competition between forward and back reactions, using the RRKM equation we can derive the expression: $k_2/k_{-1} = N_{\text{out}}/N_{\text{in}}$, i.e. the ratio of the sum of states of the critical configuration in the exit and entrance channels.

Golden and coworkers have incorporated available rate constant measurements and new experimental work to construct an optimized RRKM model of this reaction.¹¹ This model shows that at room temperature the ratio of the forward to back rate is 1.3 in the low pressure limit (i.e. absence of k_3). For a given total reaction energy, the sum of states of the exit critical configuration is greater than for the entrance critical configuration. For DOCO the situation is reversed, the ratio of the forward to backward reaction rate is 0.053 (low pressure limit). It is interesting to note that the ratio of the forward to backward unimolecular dissociation rates drops by a factor of 25 for the deuterated reaction. Associated with the critical configuration of the entrance or exit channel is a zero point energy (ZPE); this energy comes from the total energy of the adduct. An examination of the species involved reveals that for $\text{CO} + \text{OH}$, the zero point energy of the entrance critical configuration (CC) is greater than that of the exit CC by about 130 cm^{-1} . For $\text{CO} + \text{OD}$ the situation is reversed, the ZPE of CC_{in} being about 100 cm^{-1} less than the ZPE of CC_{out} . For a given total energy, a greater zero point energy means that there is less energy available with which to distribute among the available internal states, leading to a smaller sum of states (assuming a relatively small change in the density of states). The sum of states $N(E_t)$ includes all rovibrational states from the ground state to energy E_t , the sum of vibrational and translational energy for the critical configuration. The reason that $k_2/k_{-1} = N_{\text{out}}/N_{\text{in}}$ decreases upon deuteration is that due to the relative change in internal energy of 230 cm^{-1} , the sum of states in the forward CC becomes much smaller than the sum of states in the CC for back reaction. Accordingly $k_{\text{OH} + \text{CO}}/k_{\text{OD} + \text{CO}} \sim 4$.

In order to provide a conceptual framework for the effect of isotopic substitution on the competition between unimolecular product channels, we have considered a system with a specific total energy. In the laboratory a given reaction rate may represent a thermal distribution of reagent energies, and $k(T)$ is the pertinent function, not $k(E)$. Several authors have developed RRKM models of isotope effects in atmospherically relevant systems, including $\text{OH} + \text{CO}$ and $\text{OH} + \text{SO}_2$.^{11,12} A secondary kinetic isotope effect (KIE) is observed when the substituted atom is not adjacent to the bond being broken or formed. We note that in the CO reaction the secondary kinetic isotope effect (C^{18}O) is equal in magnitude to the primary KIE (^{18}OH or ^{13}CO).^{13,14}

A series of studies have brought the importance of non-methane volatile organic carbon species to the attention of the atmospheric community. Several intriguing examples have recently been reported in the literature. Rudolph *et al.* have determined the carbon kinetic isotope effect for OH reaction with a series of non-methane hydrocarbons.¹⁵ The kinetic isotope effect is seen to depend on the number of carbon atoms in the molecule. For alkenes, ϵ -values ranging from roughly 2‰ for carbon numbers >5 , to quite high values for smaller compounds (propene = 12‰ and ethylene = 16‰). These effects are much larger than can be explained by the variation of collision frequency with mass.

The magnitude of the observed kinetic isotope effect differs between saturated and unsaturated hydrocarbons—as a group unsaturated hydrocarbons exhibit ϵ 's that are a factor of 2 to 3 higher than saturated hydrocarbons. The OH KIE is thus linked to the mechanism of the reaction, addition for unsaturated systems vs. abstraction for saturated hydrocarbons. The kinetic isotope effect in the reaction between ethane and hydroxyl radicals has been proposed as an explanation for the observed

difference in isotopic composition of ethane from urban air samples *vs.* remote locations.¹⁶ Rudolph has developed a method using isotopic fractionation as an 'isotopic hydrocarbon clock' for determining the extent of photochemical processing of VOCs.¹⁵

4.3 Association reactions and 'mass independent' isotopic fractionation

The mechanism of an association reaction resembles that of an adduct forming reaction, except that the adduct itself is the product. Again, there is the possibility that the nascent adduct will decompose into reagents or possibly *via* a different channel, and a competition with the rate of collisional quenching.

Most of the processes that have been considered up to this point have a simple mass relation. For these mechanisms, the relative effect of say an ¹⁸O substitution will be twice the effect of a ¹⁷O substitution. Because of this relationship, these effects are sometimes termed 'mass dependent.' In contrast, puzzling 'mass independent' effects have been observed in several reactions. The first such reaction was discovered in 1981 by Mauersberger, who noted that ¹⁷O and ¹⁸O are about equally enriched in samples of stratospheric ozone (see Mauersberger *et al.*, and references therein).¹⁷ Subsequent laboratory experiments by Thiemens' group confirmed the unexpected enrichment of oxygen isotopes in ozone.¹⁸ For small chemical fractionations (<20‰) the isotope ratios in a three isotope system are an approximate linear function of the differences in reciprocal masses of the isotopomer species. Looking at molecular oxygen we have the following mass dependent relationship between isotopomers ¹⁶O¹⁷O and ¹⁶O¹⁸O:

$$\frac{\delta^{17}\text{O}}{\delta^{18}\text{O}} \approx \frac{\frac{1}{32} - \frac{1}{33}}{\frac{1}{32} - \frac{1}{34}} = 0.515 \quad (19)$$

Depending on molecular mass the mass dependent isotopic fractionation of oxygen containing molecules thus varies between $\delta^{17}\text{O}/\delta^{18}\text{O} \approx 0.529$ for atomic oxygen and $\delta^{17}\text{O}/\delta^{18}\text{O} \approx 0.5$ for high molecular mass species. For a more thorough discussion, the reader is referred to the recent paper by Young, Galy and Nagahara.¹⁹

Examples of mass dependent fractionation processes can be found almost everywhere, for example diffusion-limited reactions, and equilibrium across a phase boundary. The isotopic composition of terrestrial oxygen (O₂ in air, ocean water, basaltic rock...) in most cases closely follows the distribution that would be expected from a solely mass dependent processes.

Mass independent fractionation (MIF) denotes processes that give rise to changes in isotopic composition in a way that is not mass dependent as outlined above. For example in the Allende meteorite there have been observed C and Al inclusions with $\delta^{17}\text{O} \approx \delta^{18}\text{O}$.¹⁸ The departure from mass-dependence is expressed in quantitative terms (*e.g.* for O):^{14,19}

$$\Delta^{17}\text{O} \equiv \delta^{17}\text{O} - 0.52\delta^{18}\text{O} \quad (20)$$

As soon as $\Delta^{17}\text{O}$ departs significantly from zero, MIF is taking place. In the literature a number of systems with mass independent fractionation have been described, including the formation of O₃,^{2,17,20} the reaction of CO with OH,^{13,14} the photolysis of N₂O,²¹ and the photolysis of CO₂ and its reaction with O(¹D).^{17,22} some of these processes are discussed in the recent review by Weston.²⁰

The first laboratory results showed that the ozone formation reaction (recombination of oxygen atoms and O₂ molecules) gives rise to an enrichment in the heavy isotopes in ozone that is about equal for ¹⁷O and ¹⁸O. The latest experimental results on the ozone formation reaction show highly variable rate

coefficients for the individual isotopologues of O₂ and O.² The results showed that light oxygen atoms react quickly with heavy O₂ and that ¹⁸O atoms react more slowly with the different O₂ species (see Table 2). The overwhelming effect is that the

Table 2 Rates of recombination for ozone isotopomers²

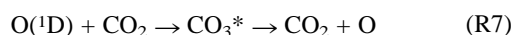
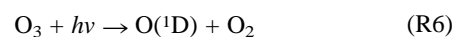
Some relative rate coefficients for different ozone formation processes:	
Reaction	Rate coeff.
¹⁶ O + ¹⁶ O ¹⁶ O	1
¹⁷ O + ¹⁶ O ¹⁶ O	1.03
¹⁸ O + ¹⁶ O ¹⁶ O	0.93
¹⁶ O + ¹⁸ O ¹⁸ O	1.53
¹⁸ O + ¹⁶ O ¹⁸ O	1.01

recombination rates are correlated with the zero point vibrational energy of the oxygen molecule.

These experiments demonstrate that the recombination reaction itself is responsible for the isotopic enrichment. Further, for ¹⁶O and ¹⁸O, the reaction ¹⁶O + ¹⁶O¹⁸O may form symmetric (¹⁶O¹⁸O¹⁶O) or asymmetric (¹⁶O¹⁶O¹⁸O) molecules, and it has been suggested that the missing rotational levels of the symmetric species will play a role in the product distribution. Sehested *et al.* were the first to show that symmetry alone could not explain the observed relative recombination rates.²³ Subsequent experiments have confirmed this finding, and demonstrated how the relative recombination rates are dependent on the temperature and pressure of the reaction, and the nature of the bath gas.

Recently Gao and Marcus published a detailed theoretical analysis of the reaction that can explain the observed isotopic distributions.²⁴ The model emphasizes two aspects in order to explain the unconventional isotopic fractionation. First, RRKM theory is used for recombination reactions, with an empirical correction for nonstatistical behavior that is larger for symmetric isotopomers. The correction factor models the proposed difference in the accessibility of states that are coupled to the exit channels depending on whether the triatomic excited molecule is symmetric or asymmetric. Because there are fewer dynamical coupling terms in the symmetric triatomic molecule than in the asymmetric one, the speed of reaching the exit channels is supposedly higher in the symmetric case. Second, the model includes a partitioning effect for the dissociation of vibrationally excited asymmetric ozone molecules formed from the recombination. The dissociation channel displaying the lower zero point energy will have a greater probability of being employed. Conversely, a system entering from the low energy side of the potential has a longer lifetime over which to be collisionally quenched.

The anomalous isotopic composition of ozone can be transferred to other atmospheric molecules, and used to measure the extent of interaction of a given species with stratospheric air. For example:^{17, 22}



The oxygen isotope signature is likely to be found in chemical systems tightly coupled to ozone, like NO_x, ClO_x and HO_x. Röckmann and coworkers have noted that the signature in NO_x may also be transferred to stratospheric nitrous oxide through the reaction NH₂ + NO₂ → H₂O + N₂O.²⁵

Another example of a process with MIF is the reaction of OH radicals with CO. The $\Delta^{17}\text{O}$ value has been shown to be inversely correlated to the CO concentration in ambient air.^{14,18} The extent of mass independent fractionation of CO can therefore be used as a measure for local OH radical concentrations.¹⁴ Relative rates for a number of the isotopologue reactions were recently determined.¹³

4.4 Dynamical models

In addition to the statistical models that have been discussed (transition state and RRKM theory), dynamical models of chemical reactions can be constructed. Theoretical calculations of chemical reaction rates can be made on the basis of a statistical or a dynamical approach. Dynamical models rely on calculating collision trajectories along the potential energy surface of the reaction. The reacting species are treated as hard spheres that collide, which leads to reaction if the energy of the system has the minimum value and any orientational requirements are met. In this type of model the dynamical differences between isotopomers are taken into account but changes in the PES that arise from isotopic substitution are not taken into account. Isotope effects that originate in tunneling through the reaction barrier can however be treated if the theory extends to these effects, for example in the CO + OH reaction. This requires at least some of the degrees of freedom in the system to be treated quantum mechanically.²⁶

4.5 Collisional transfer of energy

It has been noted that the chemical composition of the atmosphere is not at equilibrium. In addition, due to the absorption of light or chemical reaction, non-equilibrium distributions of translational, rotational, vibrational and electronic states can occur, especially in the upper atmosphere. These non-thermalised distributions can have important implications for chemical reactivity. Isotopic substitution can play an important role not only in the reactivity, but also in the lifetimes of these states. For example, the rates of processes involving intermolecular energy transfer depend on the match between the energy levels of the two systems. Isotopic enrichment resulting from collisional transfer of vibrational energy has been discussed by Coletti and Billing.²⁷ It is important to note that collisional quenching of vibrational states is rapid in the lower atmosphere, producing thermal distributions of vibrational states.

4.6 Enzyme-catalysed reactions

Unique isotopic signatures are often associated with enzyme-catalysed reactions. Examples include photosynthesis and the microbial production of nitrous oxide in the ocean and soils. Photosynthesis prefers ¹²CO₂, and leads to an enrichment of ¹³C in the remaining CO₂ gas, and a depletion in the stored carbon. Biomass therefore has a negative $\delta^{13}\text{C}$ value and the $\delta^{13}\text{C}$ value of marine carbonates is similar to that of atmospheric CO₂. Carbon stored in coal and oil is also depleted in ¹³C. Plants can be categorized as C₃ plants, which include most trees or C₄ plants, such as common marsh grasses and crops like corn and millet. The C₃ and C₄ labels refer to how these classes of plants assimilate carbon dioxide. As C₃ and C₄ photosynthesis are two biochemically different processes the carbon stored in the plants has different isotopic signatures; C₃ photosynthesis leads to a larger depletion of ¹³C in the stored carbon than does C₄ photosynthesis.²⁸

The $\delta^{13}\text{C}$ value of atmospheric CO₂ can therefore be used to trace the source, as CO₂ from a fossil fuel source will be depleted in ¹³C relative to CO₂ from plant respiration.²⁹ Likewise, $\delta^{13}\text{C}$ can provide clues about the sinks of CO₂ and their seasonal variations. Photosynthesis leads to an enrichment of ¹⁸O in the residual CO₂ compared to CO₂ originating from fossil fuels which means that these two sources can be distinguished.

In methane, the $\delta^{13}\text{C}$ value can likewise be employed to differentiate between methane from biomass burning and methane from biological sources, as the methane from plant sources such as rice paddies is depleted in ¹³C relative to the

methane from biomass burning. Atmospheric $\delta^{13}\text{C}$ values are lower than the $\delta^{13}\text{C}$ values of biological methane because of a fossil fuel contribution and because methane oxidation leads to an enrichment of ¹³C.

The greenhouse gas nitrous oxide is produced by bacteria in the soil and oceans that are involved with nitrogen fixation and release. N₂O produced by agricultural soil is depleted in ¹⁵N and ¹⁸O relative to other sources.^{25,30,38}

5 Photolysis

Photolysis is an important sink for many atmospheric trace gases. The stratospheric ozone layer largely prevents sunlight at wavelengths shorter than 300 nm from reaching the troposphere. Tropospheric photolysis of molecules such as H₂CO, O₃ and NO₂ therefore involves visible and UV-A radiation. Molecules that are slightly more photostable such as the CFCs, N₂O, OCS and O₂ are dissociated in the stratosphere, often in the 'UV window,' a region around 205 nm where a gap between the absorptions of O₂ and O₃ allows energetic solar photons to penetrate into the lower stratosphere (see for example Minschwaner in ref. 31). Thus regions of the electromagnetic spectrum important to trace gas photolysis are characterized by rapid changes in the actinic flux with wavelength. When this is convoluted with the relatively small shifts in photolysis cross section resulting from isotopic substitution, significant changes in the photolysis rate of an isotopically substituted compound can result.

The photolysis rate j (molecules cm⁻³ s⁻¹) of a molecule over the wavelength interval λ_1 to λ_2 depends on the number density of the gas n (molecules cm⁻³), the spectral flux $I(\lambda)$ (photons cm⁻² s⁻¹ nm⁻¹), the absorption cross section of the molecule $\sigma(\lambda)$ (cm²) and the photolysis quantum yield $\phi(\lambda)$.

$$j = n \int_{\lambda_1}^{\lambda_2} \sigma(\lambda)\phi(\lambda)I(\lambda)d\lambda \quad (21)$$

Some processes have more than one product channel, for example the molecular and radical product channels in the photolysis of formaldehyde. For many small atmospheric molecules, the photolysis quantum yield is unity.

Herzberg described the effect of isotopic substitution on the origin of an electronic transition between two bound electronic states. Since the potential energy surfaces themselves are not affected by isotopic substitution, the shift in the spectrum of an isotopic species is determined by shifts in the rovibrational energy levels of the lower and upper potentials. Since most excited states are more weakly bound than the ground state, this will typically result in larger shifts for the ground state levels. The upper limit for the shift, in the absence of other effects depending on nuclear mass, is simply the change in zero point vibrational energy on the lower surface. Thus labeling a molecule with a heavy isotope will result in a shift in the absorption spectrum to higher energy.

The transition intensity can be characterized by the square of the transition dipole matrix element. The dipole operator is used to determine the intensity of the electromagnetic transition between two potentials. If the transition dipole is assumed not to change with nuclear coordinates then the spectrum can be described by Franck-Condon factors or the 'reflection principle.' The usual effect is for the absorption band to be blue shifted for heavy isotope substitution. To give some examples, as summarized by Kaye,³² the absorption of CH₄ at 140 nm is shifted to 136 nm in CD₄, and the absorption of H₂O at 185 nm is shifted to 180 nm in D₂O. In contrast, no discernable shifts are seen in the UV spectra of the pairs CH₃Br/CD₃Br and C₂H₄/C₂D₄, systems in which the chromophore is not as tightly coupled to the site of substitution.

An interesting example is given by nitrous oxide. In the mid-1990s it was noted that the sources of nitrous oxide were isotopically light compared to the mean atmospheric composition, and, that photolysis of nitrous oxide did not result in isotopic enrichment. It was proposed that the imbalance in the isotope budget was the result of *in-situ* photochemical sources of nitrous oxide, for example $\text{OH}^* + \text{N}_2 \rightarrow \text{N}_2\text{O} + \text{H}$. In 1997 Yung and Miller estimated the change in absorption cross section of the isotopic species of nitrous oxide using the zero point energy theory. This work demonstrated that significant photolytic enrichments were to be expected, and that for photolysis in the stratosphere heavy isotope analogues and isotopomers have a longer lifetime than light species, thus balancing the isotopic budget.³³ Subsequent experiments demonstrated that the true enrichments were a factor of two larger than predicted by the ZPE theory.

There are a number of reasons why the zero point energy model under predicts the observed enrichments.²¹ The most important concerns the variation of the transition dipole moment with nuclear coordinates. The main transition in the 183 nm band of N_2O is from the sigma ground state to a delta excited state. This transition is forbidden, but becomes weakly allowed as the molecule bends. Further, the excited state surface has a steep slope along the bending coordinate, thus, bending of the ground state molecule gives more favorable Franck–Condon factors. The overall effect is that the transition dipole surface slopes upward as the molecule bends. The bending vibrational wavefunction of a light isotopomer has a larger amplitude than a heavy isotopomer, giving the electronic absorption a larger intensity over the whole absorption band. Instead of shifting the absorption spectrum in energy, it is shifted in intensity. A first principles model has been constructed based on the absorption cross section of each isotope analogue in each of the first three bending vibrational states, and achieves reasonable agreement with the available laboratory and stratospheric enrichment data.²¹ The budget of nitrous oxide is discussed in greater detail in Section 6. Isotope effects in atmospheric photolysis is the subject of a recent paper by Miller and Yung.³³ Recent work has considered the photolysis of isotopic analogues of water and carbonyl sulfide.^{33,34}

Many atmospheric photolysis processes involve predissociation. In these systems, the lifetime of the excited state is long enough to give rise to a structured absorption spectrum, showing for example vibrational progressions. The lifetime of the metastable state is controlled by curve crossings onto dissociative potential energy surface(s). The rate of this decay depends on the proximity of the system to the curve crossing. For some systems, for example CS_2 , the fluorescence lifetimes of individual rovibrational states are known to vary by a factor of 10^5 . Since isotopic substitution changes the energy levels, some may become closer or farther away from the curve crossing, resulting in dramatic changes in the lifetime. The phenomenon is described for example in the work of Govers *et al.* on N_2^+ from 1975.³⁵ This effect has been exploited in recent research on CO_2 in the atmosphere of Mars and early Earth by Thiemens and coworkers.²² Recent work on CS_2 suggests that the mass independent fractionation of sulfur isotopes is due to Franck–Condon and vibronic coupling effects on nonradiative decay and intersystem crossing rates for the lowest excited states.³⁶

6 Stable isotope analyses of the biogeochemical cycles

The recently issued Intergovernmental Panel on Climate Change (IPCC) report has examined the available literature to assemble source and sink budgets for atmospheric gases such as methane, nitrous oxide and carbon dioxide that are involved

with global change.³⁷ These budgets form the basis of any effort to regulate the emission of greenhouse gases, but they contain significant uncertainties. For example according to the report the total emission of nitrous oxide is somewhere between 6.7 and 36.6 Tg N yr⁻¹. One method for decreasing this uncertainty is to construct an isotope budget, based on the mass balance equation, $dN/dt = P - L$. The change in the mass of a gas in the atmosphere is equal to the imbalance between production and loss. This method will depend on characterizing the ‘isotopic signature’ of the sources and the sinks of a given gas. Atmospheric models of all levels of complexity are used to model physical and chemical fractionation processes, from zero-dimensional ‘box’ models, to one and two dimensional models,^{8,33} to three dimensional models.³⁸ We will now briefly consider several sources of isotopologues and isotopomers of atmospheric trace gases, and conclude this Section by giving several examples of isotopomer budgets of atmospheric gases.

6.1 Carbon

The stable isotope ratios of carbon and oxygen can provide clues about the biogeochemical cycles. Biogenic CH_4 and CH_4 from biomass burning have different ratios of ^{13}C to ^{12}C so methane from these sources can be traced by isotopic analysis. Enzymatic reactions favor lighter isotopes, so methane that is biological in origin is depleted in ^{13}C relative to the ^{13}C standard (carbonate in Pee Dee Belemnite). Methane from biomass burning has a relatively higher content of ^{13}C . The most common application of methane isotopic tracing is to distinguish biological sources from fossil sources. ^{13}C from combustion sources corresponds to the distribution in fossil fuels, which is similar to the standard. ^{18}O is enriched by of 23.5‰ relative to ^{16}O in oxygen containing compounds originating from combustion. The methane budget in the atmosphere has been improved considerably by consideration of the isotopic signature of the reactions with OH, O(¹D) and Cl.⁸

While the atmospheric carbon cycle is essentially a ^{12}C cycle, the minor isotopes ^{13}C and ^{14}C (see Table 1) can be used to show the effects of physical and chemical processes.²⁹ Fossil fuels have low $\delta^{13}\text{C}$ compositions, biasing the $\delta^{13}\text{C}$ observed in atmospheric CO_2 . A significant fraction of CO_2 is removed from the atmosphere by plants during photosynthesis. This process is more rapid for $^{12}\text{CO}_2$ than $^{13}\text{CO}_2$, and ^{13}C becomes enriched in the CO_2 left in the atmosphere. CO_2 is also removed from the atmosphere by solvation in the oceans—this process does not have a strong isotopic signature. Therefore $^{13}\text{C}/^{12}\text{C}$ ratios provide a good way of determining the partitioning of the atmospheric CO_2 sink between the terrestrial biosphere and the ocean. During the twentieth century the relative concentration of ^{13}C in atmospheric CO_2 has decreased, as more CO_2 from ^{13}C -poor fossil fuels is added to the atmosphere. About 1/6 of atmospheric CO_2 originates from the oxidation of CO by OH radicals so the isotope effect in this reaction as well as the isotopic composition of atmospheric CO makes a significant contribution to the CO_2 signature.

^{14}C is a rare isotope produced by the interaction of solar particles with atmospheric nitrogen. About 10 g of ^{14}C are produced each year. In addition large quantities of ^{14}C were produced in the 1960s by nuclear bomb tests in the atmosphere. The half life of ^{14}C is 5730 years, and thus it is absent from fossil carbon. The decreasing ratio of radioactive ^{14}C to ^{12}C in atmospheric CO_2 and CO is evidence of the introduction of large amounts of fossil fuel CO_2 .

6.2 Sulfur

As shown in Table 1, several stable sulfur isotopes occur in nature. We will consider the stratospheric sulfate aerosol layer,

known as the Junge layer named after Christian Junge who discovered it. These particles are important to global change because they reflect incoming sunlight. An increase in sulfuric acid aerosol increases the albedo, cooling the planet. At the same time, these particles contribute to mid-latitude ozone depletion by changing the partitioning of species within the chemical families that destroy ozone. It is therefore germane to determine whether anthropogenic activity perturbs the Junge layer. In 1976 Paul Crutzen identified the photolysis of OCS as a source of stratospheric sulfate. In addition, SO₂ is transported into the stratosphere by convection in the tropics. Intense volcanic eruptions periodically inject large amounts of SO₂ into the stratosphere that is converted into sulfuric acid by a series of reactions beginning with oxidation by OH.

Leung *et al.* have characterised the isotopic signature of the SO₂ + OH reaction using an RRKM model of the reaction.¹² This study results in an accurate determination of δ³⁴S throughout the Mt. Agung volcanic eruption. In addition, in analogy to nitrous oxide it is expected that the photolysis of carbonyl sulfide will result in an isotopic signature that can be observed in the end product sulfate.²¹ The distribution of OC³⁴S in the stratosphere has been determined by Toon and coworkers.²⁴ Experiments are necessary to determine the photolysis cross section of the OCS isotopologues, and to confirm the theoretical predictions concerning the isotopic signature of the SO₂ oxidation reaction.

7 Conclusion

Isotopic analysis has resulted in significant advances in our understanding of atmospheric chemistry and global change. Many examples have been given, including CO₂, N₂O and CO. We anticipate further progress with for example characterizing emissions and transformations of biogenic volatile organic carbon species. Another use of stable isotope analysis that holds great promise is the analysis of the historical isotopic enrichments of trace gases contained in air trapped in glaciers. In this way, a historical record of the emissions sources of for example carbon dioxide, methane and nitrous oxide can be constructed.

This review has discussed the effect of isotopic substitution on gas-phase reaction rates, while largely ignoring their effect on condensed phase reaction rates, beyond the effect of isotopic substitution on the rate of diffusion. Heterogeneous reactions are known to be of great importance in the atmosphere. We anticipate that this subject will be addressed by experimentalists in the near future.

The anomalous enrichment of oxygen isotopes in stratospheric ozone discovered by Mauersberger has inspired workers in this field for many years.^{2,17,18} It is interesting to note how the field has advanced from a state in the 1980s where isotope effects in stratospheric ozone were perhaps a curiosity, to the 1990s where the phenomenon was the subject of intense theoretical debate,^{20,24} to the current state of knowledge, where we are starting to apply knowledge of the unique isotopic signature of oxygen in ozone to analyse the interaction between ozone and other atmospheric gases, like CO₂, N₂O, and NO₂.^{17,25} Some of the features of the ozone formation reaction can be found in the CO + OH reaction, where the exit and entrance barriers of the HOCO adduct are of similar height.^{13,14,26} This gives rise to anomalous isotope effects arising from small changes in the zero point energy in the entrance or exit channel. The isotope effects in a large number of reaction systems, especially photolysis and adduct-forming and association reactions, have yet to be explored.

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