

A MECHANISM OF THE STRANGE ISOTOPIC FRACTIONATION OF OXYGEN FOUND IN METEORITE AND LABORATORY

J. Yang and S. K. Kim

Dept. of Physics, Ewha Womans Univ., Seoul 120-750

K. S. Soh

Dept. of Physics, Seoul Nat'l Univ., Seoul 151-742

J. H. Yee

Dept. of Physics, Yonsei Univ., Seoul 120-749

S. W. Kim, K. H. Kim and K. W. Yoo

Dept. of Science Education, Ewha Womans Univ., Seoul 120-750

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Abstract

The thermodynamic nonequilibrium distribution of the vibrational states of ozone coupled with anharmonic predissociation produces an unusual isotopomeric pattern of oxygen molecules. The model presented here explains the experimental data obtained from the electric discharge of oxygen gas to produce ozone condensed on a quartz wall at 77K.

I. Introduction

Oxygen is one of the most abundant elements in the solar system. Isotopic studies of oxygen have provided considerable information on the origin and history of solar system material. Relatively enriched ^{16}O in some primitive meteorite samples (Clayton *et al.* 1973) and the importance of ozone in earth environment (Okabe 1978) have stimulated considerable experimental and theoretical studies. For example, ^{16}O enrichment in meteorite samples was interpreted as an input of pure ^{16}O nucleus produced in exploding stars such as supernova. However, it is very important to determine that the anomaly can also be produced by other mechanisms.

Several attempts have been made to find such possibilities (Arrbenius *et al.* 1979, Heidenreich and Thiemens 1983, Navon and Wasserburg 1985, Heidenreich and Thiemens 1986). When an oxygen gas of atmospheric composition was discharged to form an ozone molecule, isotopic fractionations resembling the pattern found in meteorites were obtained (Heidenreich and

Thiemens 1983, 1986, Yang and Epstein 1987a, b). Models such as self-shielding, molecular symmetry of O_2 , molecular symmetry of O_3 , and the vibrational relaxation of O_2 into the ground state of O_2 have been considered. Yang and Epstein(1987a, b) reported that the discharge of O_2 molecules of various isotopic compositions at various excitation energies produced very unusual isotopic fractionation patterns which can not be explained by any models suggested so far. They presented a preliminary model which is based on the anharmonic predissociation processes. Here, the model is presented in detail and more theoretical considerations are made.

II. Nomenclature and Setup

Let's consider an oxygen gas system in which a part of oxygen molecules(O_2) are dissociated by a discharge and ozone molecules(O_3) are produced by the recombination of the atomic oxygens and the oxygen molecules. The reaction product(O_3) will have different isotopic composition compared with the starting oxygen(O_2). Isotopic fractionations occurring during these molecular reactions are studied in this paper.

In the experiment(see Yang and Epstein 1987a, b for experimental full details), a high AC voltage is applied to the neck of a quartz tube which contains oxygen gas of pressure P_0 . The bottom part of the tube is immersed in a liquid nitrogen, 77K. Electric discharge produces radical oxygen atoms which combine with molecular oxygen to form a vibrationally hot ozone in a certain excited state. This excited O_3 will experience vibrational relaxation by collision with other molecules to make stable O_3 and eventually condense on the cold wall. If the excited O_3 does not collide with other molecules, it will predissociate to form O_2 and O with a certain probability(Herzberg 1966). The isotopic composition of the condensed ozone will mainly be determined by the vibrational temperature θ_v (Treanor *et al.* 1968), predissociation rate $D_{n,v}$ (Harris 1963), and collision time t between O_3 and the other molecules. Here, n is an electronic state quantum number and v is a vibrational quantum number.

In order to describe the change of the isotopic composition during the reaction, it is convenient to use normalized abundance of each isotopic component. The isotopomeric abundance of O_2 of mass i is denoted by R_i where $\sum_{i=32}^{36} R_i=1$. Here the term, isotopomers, refers to the molecules composed of a given set of chemical elements, but of different atomic masses. Since the reactions produce ozone, this abundance R_i should be transformed to the normalized isotopomeric abundance of O_3 of mass j . We will use the symbol R_j with $\sum_{j=48}^{54} R_j=1$ for the abundance. Note that

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i refers to O₂ species and j refers to O₃ species. R_i can be obtained from the isotopic composition of ¹⁶O, ¹⁷O, and ¹⁸O assuming that the statistical isotopic partitioning is valid. R_i values are useful in experimental data analysis, because O₂ gas is used in mass spectrometric measurement and R_i values are useful in theoretical modeling.

Now it is necessary to describe how the isotopic compositions of various gases are different from each other. We will use initial oxygen gas before the gas discharge as a standard. The initial isotopomeric composition of O₂ is denoted by R_i⁰. It is convenient to define the change of ratios, δ_j and δ_i in per mil(‰), with respect to standard isotopomers. j=51 and i=34:

$$\delta_j = 1000(R_j/R_{51} - R_j^0/R_{51}^0)/(R_j^0/R_{51}^0) \dots\dots\dots (1)$$

$$\delta_i = 1000(R_i/R_{34} - R_i^0/R_{34}^0)/(R_i^0/R_{34}^0) \dots\dots\dots (2)$$

Here R_i⁰ and R_i can be measured mass spectrometrically, allowing δ_i values to be compared with the theory.

III. Predissociation Model

The condensation rate of ozone will be proportional to the probability of the excited O₃ to form stable ozone by collisional relaxation with other molecules(O₂, O₃) and the cold wall as well as the collision rate of ozone on the wall, Φ. When the typical collision time is t_n, we may write the condensation rate of ozone isotopomer j as

$$R_j \propto \Phi_j \exp(-t_n \sum_n D_{n,j}) \dots\dots\dots (3)$$

where D_{n,j} is the predissociation rate of excited ozone (j) at energy level (n, v) and $\sum_n D_{n,j}$ could be written as 1/τ_j where τ_j is the mean lifetime of ozone isotopomer j. If the velocity distribution is similar to the Boltzmann distribution, Φ_j is proportional to m_j^{-1/2} or j^{-1/2} and t_n is proportional to j^{1/2}. When we take a derivative of eq.(3), we obtain

$$\frac{R_j - R_{51}}{R_{51}} = -\frac{1}{2} \frac{j-51}{51} - \frac{1}{2} \frac{t_{51}}{\tau_{51}} \frac{j-51}{51} + \frac{t_{51}}{\tau_{51}} \frac{\tau_j - \tau_{51}}{\tau_{51}} \dots\dots\dots (4)$$

Since all O_3 produced eventually condenses on the wall, the first term can be omitted. Eq.(4) then becomes

$$\frac{R_j - R_{51}}{R_{51}} \cong \left(-\frac{j-51}{102} + \frac{\tau_j - \tau_{51}}{\tau_{51}} \right) \frac{t_{51}}{\tau_{51}} \dots\dots\dots (5)$$

Two metastable ozone levels with lifetimes of several μ sec have been discovered(Hochanadel *et al.* 1968, Bevan and Johnson 1973, Rosenbery and Trainor 1974, Burton and Harvey 1977). However, there are also several electronic states with a few eV(Hay and Dunning 1977), some of which will be predissociated with lifetimes much shorter than 1 μ sec. For the case of electric discharge, the characteristic vibrational temperature θ_v of vibrational level v , probably a few eV, is much greater than translational temperature T , ~ 0.007 eV and the reactions involved will be in thermodynamic nonequilibrium. Therefore, the distribution of the vibrational levels of the excited ozone will be very different from a Boltzmann distribution and from the Landau-Teller theory(Treanor *et al.* 1968, Landau and Teller 1936). Ozone molecules will be highly populated at higher vibrational states and such a distribution depends very much on the degree of anharmonicity of the vibrational potential(Treanor *et al.* 1968).

We might estimate $(\tau_j - \tau_{51})/\tau_{51}$ considering the detailed structure of ozone. Three oxygen atoms stretch with angles of $100-124^\circ$ for most excited ozone states(Hay and Dunning 1977). In the first approximation, we may say that vibrational frequencies of ozone (j) are proportional to $j^{-1/2}$. There are two kinds of molecular symmetry of isotopomeric O_3 , C_{2v} and C_s . Each molecular symmetry has two different molecular configurations which result in different degrees of anharmonicity. C_{2v} has X-X-X and X-Y-X and C_s has X-X-Y and X-Y-Z. The ozone isotopomers with higher j and with higher degree of anharmonicity such as X-Y-X and X-Y-Z will have smaller gap between vibrational energy levels at higher v , and thus have higher vibrational temperature, θ_v . Therefore, these isotopomers will have relatively lower populations at energy levels higher than the dissociation limit if the dissociation energy to make O_2 and O is independent of j . The lower populations mean lower dissociation rate. Therefore, the lifetime of excited intermediate ozone will depend on both the mass and the symmetry configuration of O_3 (See Appendix for the derivation of the expression in the case of thermal unimolecular dissociation).

When we take account the mass dependence of ω_v , $j^{-1/2}$, we can write

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$$\frac{\tau_j - \tau_{51}}{\tau_{51}} \cong \frac{1}{2} \frac{j-51}{51} p_j + q_j \dots\dots\dots (6)$$

Where p_j is a parameter which relates the vibrational frequency with the lifetime of O_3 and q_j is a parameter which is from the degree of anharmonicity of the O_3 configuration. If we assume p_j is p , independent of j , and q_j is 0 for the reference isotopomer, 16-17-18, $-q$ for O_3 of two identical O atoms, and $-2q$ for O_3 of three identical O atoms. eq. (5) becomes

$$\frac{R_j - R_{51}}{R_{51}} \cong \left[-\frac{j-51}{102} (1-p) + q_j \right] \frac{t_{51}}{\tau_{51}}$$

$$q_{46} = q_{45} = -2q, q_{49} = q_{50} = q_{53} = -q, q_{51} = 0 \dots\dots\dots (7)$$

There are some experimental data for the isotopomeric dependence of lifetimes which seem to agree with our assumption[See for example, CH_4 (Dibeler and Rosenstock 1963) and CO_2 (Newton and Sciamanna 1964)]. In principle, the parameters p_j and q_j could be calculated by predissociation theory(Harris 1963) using ab initio potential.

IV. Application of the Model

Let us compare the above theory with the experimental data of Yang and Epstein(1987b) obtained by discharging O_2 gas at a pressure of 10cmHg with a Tesla coil which produces an external AC voltage of 20kV. The composition of the enriched oxygen gas used was 79.1% ^{16}O , 6.8% ^{17}O and 14.1% ^{18}O (cf. air oxygen:99.76% ^{16}O , 0.038% ^{17}O , 0.200% ^{18}O). Therefore, R_i^0 values are 0.626, 0.108, 0.227, 0.0192, 0.0198 and R_j^0 values are 0.495, 0.128, 0.275, 0.0458, 0.0490, 0.0041, 0.0028. The measured δ_i values are $\delta_{32} = -8.7$, $\delta_{33} = 10.1$, $\delta_{35} = 18.9$ and $\delta_{36} = 7.1\%$. From eqs. (1), (2) and (7) we can express δ_i values with p , q and t/τ :

$$\delta_{32} = 20(1-p) \frac{t_{51}}{\tau_{51}} - 710q \frac{t_{51}}{\tau_{51}}$$

$$\delta_{33} = 10(1-p) \frac{t_{51}}{\tau_{51}} + 110q \frac{t_{51}}{\tau_{51}}$$

$$\delta_{35} = -10(1-p) \frac{t_{51}}{\tau_{51}} + 810q \frac{t_{51}}{\tau_{51}}$$

$$\delta_{36} = -20(1-p) \frac{t_{51}}{\tau_{51}} + 680q \frac{t_{51}}{\tau_{51}} \dots\dots\dots (8)$$

Comparing with the experimental δ_i values we obtain

$$\begin{aligned} (1-p)t_{51}/\tau_{51} &= 0.70 \\ q t_{51}/\tau_{51} &= 0.032 \dots\dots\dots (9) \end{aligned}$$

Fig. 1 shows the experimental δ_i values along with the theoretical fit. It is rather surprising that the simplified eq. (7) explains the data well. Since the first term in eq. (6) should be about the same as the second term, we might put $p=100q$ in order to estimate an order of magnitude of each quantity in eq. (9). Eq. (9) gives $p=0.82$, $q=0.0082$, $\tau_{51}=0.26 t_{51}$. If δ_{r_1} is defined by

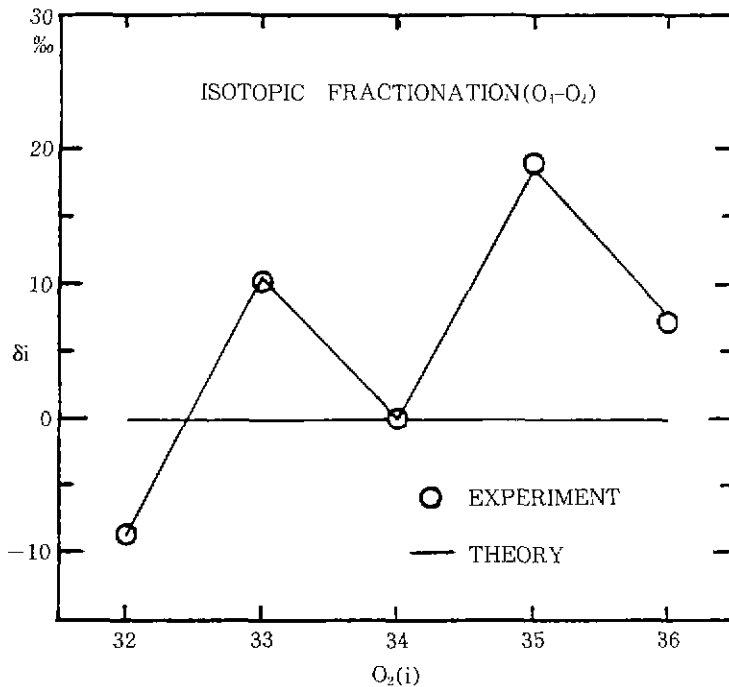


Fig. 1. Isotopomeric pattern of oxygen gas converted from ozone which was made by gas discharge of 20 kV in 10cmHg O₂ gas (79.1% ¹⁶O, 6.8% ¹⁷O, 14.1% ¹⁸O) by Yang and Epstein(1987b). δ_i value of O₂(in ‰ defined in eq. (2)) measured on an isotope ratio mass spectrometer is compared with a theoretical curve with parameters given in (9). The size of the experimental data represents 2 σ error in δ_i values.

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$$\delta\tau_j = 1000 \frac{\tau_j - \tau_{51}}{\tau_{51}} \dots\dots\dots (10)$$

$\delta\tau_j$ values becomes $\delta\tau_{48} = -41$, $\delta\tau_{49} = -24$, $\delta\tau_{50} = -16$, $\delta\tau_{51} = 0$, $\delta\tau_{52} = 8$, $\delta\tau_{53} = 8\%$ (Fig. 2).

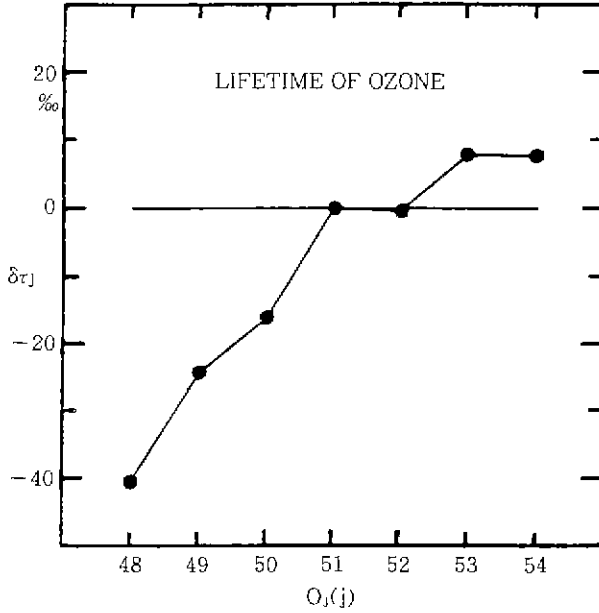


Fig. 2. Lifetime of intermediate(vibrationally excited) ozone derived from the model calculation against the mass number of O₃, j.

Now let us estimate the order of magnitude of τ . Collision time t_c is approximately $(n\sigma v)^{-1}$ where n is the density of O₂+O₃, σ is the collision cross section between intermediate O₃ and the other molecules, and v is the mean velocity of intermediate O₃. For 10 cmHg O₂ gas at 77K, t_c is approximately 10⁻⁸ sec. Therefore τ must be approximately a few n sec which is quite reasonable since the metastable states of O₃ have lifetime of several μ sec.

V. Discussion and Summary

The search for a non-nuclear mechanism which could produce oxygen isotopic anomalies observed in meteorites has produced several theories. Arrhenius *et al.*(1979) suggested the possibility that the predissociation rate is important. Navon and Wasserburg(1985) reached the con-

clusion that the self shielding mechanism is incorrect, which is consistent with our experimental data. Heidenreich and Thiemens(1985) suggested that ^{18}O enrichment is due to $\tau_{48} < \tau_{19} = \tau_{50}$. They argued that the nondegenerate rotational states of $^{49}\text{O}_3$ and $^{50}\text{O}_3$ double the number of energy states when compared with the rotationally degenerate states of $^{48}\text{O}_3$. Such an explanation is not supported by our data.

Recently Park *et al.*(1989) and Wen and Thiemens(1989) studied the non-mass dependent isotope effect occurring in the thermal decomposition of ozone by unimolecular reactions. Park *et al.*(1989) showed that the RRKM theory might explain the magnitude of isotopic fractionation observed by Yang and Epstein(1987a, b) and the dependence of the oxygen gas isotope composition used in the experiments. Wen and Thiemens(1989) observed that the isotopic fractionation of ozone by thermal decomposition depends strongly on temperature and the size of the variation was about 40%. It has to be seen that the theoretical calculation could explain experimental data for the case of thermal decomposition. However, non-equilibrium predissociation is more important for the case of discharge experiments. More experimental investigation such as Wen and Thiemens(1989) as well as more theoretical model calculation are clearly needed.

In summary, gas discharge of oxygen enriched in heavy isotopes produces an isotopomeric pattern of oxygen which has not been previously observed. The theory presented here explains the experimental data well and provides interesting lifetimes, a few n sec, of excited intermediate ozone averaged in all vibrational states. The values of τ_i depend on the mass and the symmetry of the molecular structure of O_3 , due to nonequilibrium vibrational distribution coupled with anharmonic predissociation.

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Appendix

In the case of thermal unimolecular reactions, the predissociation rate ($\sum_i D_{n,i}$) at a high pressure is proportional to Q_j^+ / Q_0 (Robinson and Holbrook 1972), where Q_j^+ is the vibrational partition function for three active degrees of freedom for activated O_3 and Q_0 is that for two active degrees of freedom for reactant O_3 . We can assume that the activated O_3 is the rigid transition state. Using Q expression in McQuarrie (1976) we obtain

$$\tau_j^{-1} \propto \frac{1 + 2\rho_j h \nu / kT [\exp(\rho_j h \nu / kT) - 1]^{-2} \rho_j \chi_{eij}}{\exp(\rho_j h \nu / 2kT) - \exp(-\rho_j h \nu / 2kT)}$$

Here, ν is an antisymmetric fundamental vibrational frequency because we choose this as a reaction coordinate, χ_{eij} is an anharmonicity constant, and $\rho_j = (m_0/m_i)^{-1/2}$ where m_0 is the molecular weight of the reference molecule, X-X-X. Since $h\nu \gg kT$ and the anharmonicity term is much less than 1, the above equation leads to

$$\tau_j^{-1} \delta \tau_j \cong -h\nu / 2kT \delta \rho_j + 2\rho_j^2 h \nu / kT \exp(-2\rho_j h \nu / kT) \delta \chi_{eij}$$

The first term gives a primary kinetic isotope effect and the second term gives a statistical effect. This equation leads to the eq. (6) with

$$\begin{aligned} p_j &\cong h\nu / 2kT \rho_j \\ q_j &\cong 2\rho_j^2 h \nu / kT \exp(-2\rho_j h \nu / kT) (\chi_{eij} - \chi_{e0i}). \end{aligned}$$

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