

Vibrational relaxation of O₃ by H₂O and D₂O

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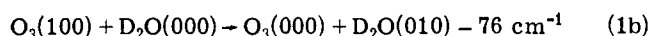
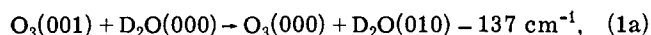
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The vibrational relaxation of laser excited O₃(001) by H₂O and D₂O has been studied over the temperature range 295–473 °K. The CO₂ laser-induced chemiluminescent reaction of NO + O₃(001) was utilized to monitor the decay rate of vibrationally excited ozone. The relaxation probability for both water isotopes has a strong inverse temperature dependence, with D₂O being four times more efficient than H₂O. The results are discussed in terms of a metastable complex model for energy transfer.

I. INTRODUCTION

The water molecule is a particularly interesting subject for energy transfer studies because of its unusual physical and chemical properties. Its ability to form strong hydrogen bonded complexes makes it an efficient quenching partner. Its small moment of inertia gives it an unusually fast rotational velocity. The large rotational constants facilitate resonant energy transfer by converting much of the energy defect into rotational energy. Finally, the very different vibrational frequencies and moments of inertia of H₂O and D₂O can produce large isotope effects.

In this paper we report the vibrational relaxation of O₃(001) by H₂O and D₂O over the temperature range 295–473 °K. It is interesting to speculate in advance as to the nature of the possible isotope effect. On the one hand, the near-resonant transitions



favor *V*–*V* relaxation by D₂O. On the other hand, high rotational velocity favors *V*–*R*, *T* relaxation by H₂O. Still a third argument¹ is that complex formation dominates the relaxation process and, since the attractive potential is the same for both H₂O and D₂O, no isotope effect is expected. Since all three arguments have some merit, it is very helpful to examine the temperature dependence of the relaxation probabilities in order to pin down the correct mechanism. Both the resonance² and complex³ mechanisms predict an inverse temperature dependence. However, the probability of resonant energy transfer also depends on the Boltzmann populations of rotational states capable of transitions with small energy defects, and these populations are likely to have different temperature dependences for H₂O and D₂O. In contrast, for the complex mechanism a similar temperature dependence is expected for H₂O and D₂O.^{3–6} Finally, if the rotational velocity plays a major role, then a positive temperature dependence is expected with a reduced Landau–Teller coefficient.^{7,8} Thus, each mechanism has a unique “signature” which contributes to the overall relaxation probability.

II. METHODS

The vibrational relaxation of ozone by the isotopes of water was observed in a temperature controlled fast flow apparatus. A mixture of NO, O₃, H₂O (or D₂O), and Ar was irradiated with a CO₂ TEA laser [180 mJ/

pulse, 1 Hz, 1053.9 cm⁻¹, *P*(12) line], which selectively excites O₃ to the *v*₃ = 1 level. The decay rate of O₃[†] was monitored by measuring the time dependence of visible NO₂ emission from the laser enhanced reaction NO + O₃[†] → NO₂^{*} + O₂. The flow apparatus and the computerized data acquisition system have been described elsewhere.⁹ Water and heavy water vapor were collected over the liquid after purification by four freeze–thaw cycles. The vapor was diluted with Ar in a 7 : 1 (Ar : H₂O/D₂O) mixture and stored in a 50 liter Pyrex bulb. Ozone was similarly stored in a 5 : 1 (Ar : O₃) dilution. The partial pressures of gases in the flow system were determined by measuring the individual flow rates and the total pressure in the reaction chamber. NO and water flow rates were measured using calibrated mass flowmeters. The ozone flow rate was calculated from the timed pressure drop in the storage bulb. The total pressure in the reaction cell was measured with a capacitance manometer. The resulting partial pressures were 2.00–2.10 Torr of NO, 0.3–0.4 Torr of the O₃–Ar mixture, and 0.0–1.0 Torr of the H₂O (D₂O)–Ar mixture, giving total flow rates of 0.19–0.40 mMole/sec.

III. RESULTS

The laser-induced chemiluminescent signal was fitted to the functional form

$$I(t) = C [\exp(-\lambda_1 t) - \exp(-\lambda_2 t)]. \quad (2)$$

As has been shown previously,⁹ λ_1 is the sum of the rates of all processes consuming O₃[†], while λ_2 is the quenching rate of NO₂^{*}. A Stern–Volmer plot of λ_1 vs the concentration of quenching gas *M* (H₂O or D₂O) has a slope equal to the observed relaxation rate constant *k_M*. A typical Stern–Volmer plot is shown in Fig. 1.

The interpretation of *k_M* is complicated somewhat by coupling between the stretching and bending modes of ozone. As discussed previously^{8,10} there are two limiting cases. Let *k_M^S* and *k_M^B* refer to the rate constants for relaxation of the stretching modes and the bending mode of O₃, respectively.¹¹ In the limit of very rapid coupling we obtain

$$k_M^{\text{obs}} = k_M^B + (k_M^S - k_M^B)\delta, \quad (3)$$

where

$$\delta = 2 \exp(-\Delta\epsilon/kT) / [1 + 2 \exp(-\Delta\epsilon/kT)]. \quad (4)$$

In Eq. (4), $\Delta\epsilon$ is the difference between the average

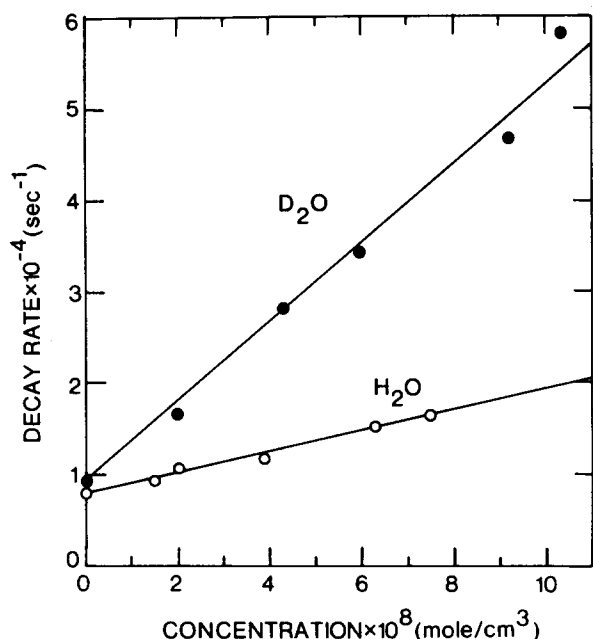


FIG. 1. Stern-Volmer plot of the relaxation of O₃ by H₂O and D₂O at room temperature.

energy of O₃(001) and O₃(100) and the energy of O₃(010). Previous experience^{10,12} suggests that reality lies about midway between these extremes.

The experimentally observed rate constants are listed in Table I. Also listed in the table and plotted in Fig. 2 are the thermally averaged transition probabilities

$$P_M(T) = k_M^{\text{obs}}(T)/k_M^{\text{HS}}(T), \quad (5)$$

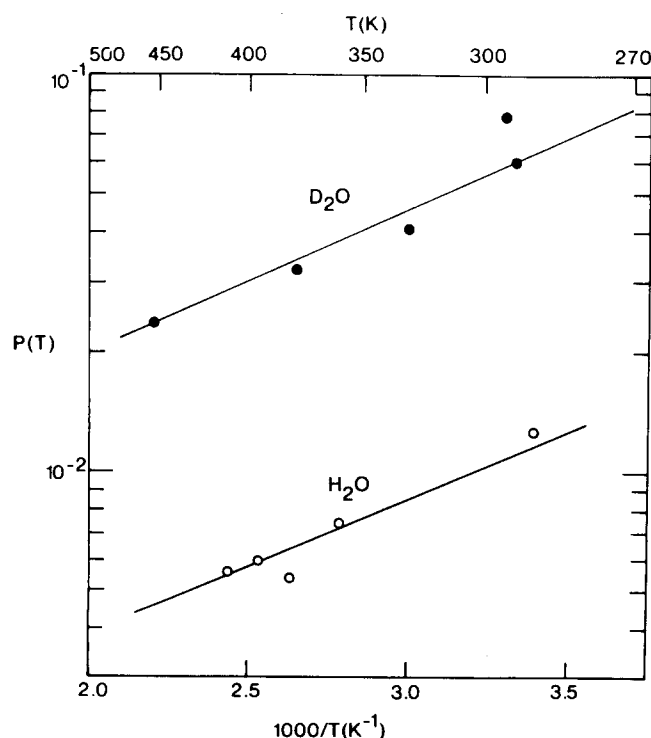


FIG. 2. Probability of relaxation of O₃ by H₂O and D₂O as a function of temperature.

TABLE I. Observed rate constants and relaxation probabilities.

	T (°K)	$k_M^{\text{obs}} \times 10^{-12}$ (cm ³ mole ⁻¹ sec ⁻¹)	$P_M \times 10^{-2}$
H ₂ O	295	2.00	1.26
	360	1.30	0.74
	380	0.97	0.54
	395	1.08	0.59
	410	1.05	0.56
D ₂ O	300	9.55	6.0
	303	12.7	7.9
	333	6.90	4.1
	377	5.51	3.2
	473	4.69	2.4

where k_M^{HS} is the hard sphere rate constant. As shown in Fig. 2, $P_{\text{H}_2\text{O}}$ and $P_{\text{D}_2\text{O}}$ both have a strong negative temperature dependence, with D₂O being approximately four times more efficient than H₂O as a quenching partner. It is convenient to fit the data to different functional forms to facilitate comparison with other systems. For an Arrhenius-like function

$$P_M(T) = A_M \exp(\epsilon_M/kT), \quad (6)$$

we obtain $A_{\text{H}_2\text{O}} = 5.8 \times 10^{-4}$, $\epsilon_{\text{H}_2\text{O}} = 1.8 \pm 0.2$ kcal/mole, $A_{\text{D}_2\text{O}} = 3.4 \times 10^{-3}$, and $\epsilon_{\text{D}_2\text{O}} = 1.8 \pm 0.3$ kcal/mole. For a power law behavior

$$P_M(T) = B_M T^{-n_M}, \quad (7)$$

we obtain $B_{\text{H}_2\text{O}} = 3.8 \times 10^4$, $n_{\text{H}_2\text{O}} = 2.6 \pm 0.3$, $B_{\text{D}_2\text{O}} = 3.8 \times 10^4$, and $n_{\text{D}_2\text{O}} = 2.3 \pm 0.4$.

IV. DISCUSSION

The most striking aspect of our data is the strong negative temperature dependence of the relaxation probabilities for H₂O and D₂O. The mechanisms most likely to cause such behavior are resonant V-V, R energy transfer and the formation of metastable complexes. While both mechanisms probably contribute to the relaxation, the identical temperature behavior of H₂O and D₂O suggests that resonances play a lesser role. Closer examination confirms this. For a resonant transition from initial state i to final state j , the thermally averaged transition probability can be written as

$$P_{ij}(T) = P_{ij}^{\text{res}}(T) X_i(T), \quad (8)$$

where $P_{ij}(T)$ is the state-to-state transition probability, and $X_i(T)$ is the mole fraction of reactants in state i . The total transition probability is a sum over i and j for all resonant transitions. For nearly resonant transitions, $P_{ij}^{\text{res}}(T)$ is only weakly dependent on the specific states involved, and to a fair approximation we may replace $\sum_{ij} P_{ij}(T)$ by $P^{\text{res}}(T) \sum X_i(T)$. Sharma and Brau² showed that for long-range electrostatic interactions $P^{\text{res}}(T)$ varies as T^{-1} . Consequently, if their theory is applicable here, most of the temperature dependence must be borne by the population factor. For D₂O, the possible resonant transitions are of the type

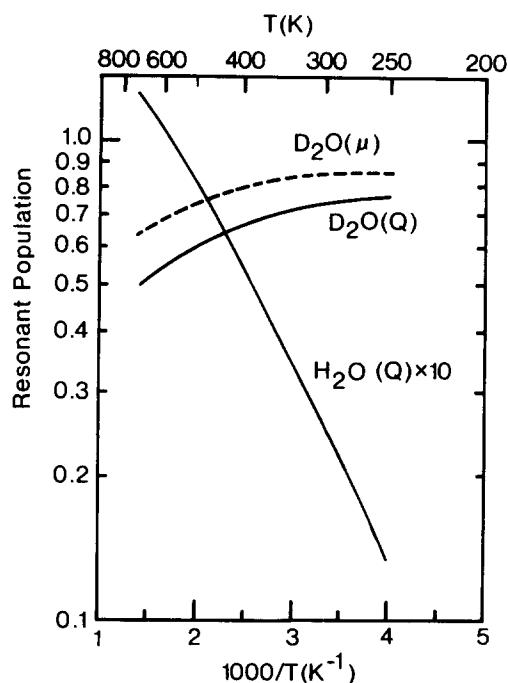
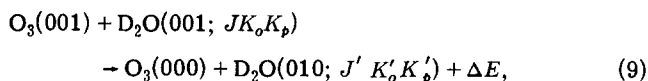


FIG. 3. Mole fractions of H₂O and D₂O molecules in rotational states that can participate in near-resonance V-V, R transitions with energy defects less than 50 cm⁻¹. The solid curves are for quadrupole allowed transitions with O₃(001) and O₃(100); the dashed curve is for dipole allowed transitions.



where $J=0, \pm 1$ and $K_o, K_p=0, \pm 1, \pm 2$, etc., for dipole allowed transitions, and $J=0, 1, 2$ and $K_o, K_p=0, \pm 2, \pm 4$, etc., for quadrupole allowed transitions.¹³⁻¹⁵ For H₂O only quadrupole transitions are near resonant. The total populations (summed over all transitions, using proper spin statistics) with $|\Delta E| < 50$ cm⁻¹ for both O₃(001) and O₃(100) are plotted in Fig. 3. It is apparent from this figure that the resonant populations of H₂O and D₂O are very different from each other and that neither has the proper temperature dependence to fit the data. Moreover, the magnitude of $P^{\text{res}}(T)$ can be approximated with the Sharma-Brau theory. Reasonable estimates¹⁶ of the transition moments of H₂O and D₂O show that the first order resonant contribution to the observed $P_M(T)$ is <1% for H₂O and <23% for D₂O. The amount of actual resonant energy transfer is substantially reduced if there is significant intermode relaxation to the $\nu_2=1$ state of ozone. Such an effect has been observed in the resonant relaxation of O₃(001) by ortho-H₂.¹⁰ We infer that the major contribution to the relaxation probability is from complex formation, which masks the role of resonant energy transfer.

The metastable complex model of vibrational relaxation is discussed in detail in the previous paper.⁴ Briefly, the microscopic rate constant for vibrational relaxation is given by

$$k(E) = v\sigma_c(E)\Gamma(E), \quad (10)$$

where E is the collision energy, v the velocity, σ_c the

capture cross section, and Γ the branching ratio for inelastic vs elastic decay of the complex. The inverse energy dependence of $k(E)$ stems from the fact that both σ_c and the complex lifetime vary inversely with E . The longer the complex lives, the greater the opportunity for O₃[†] to transfer its energy to other degrees of freedom. The common temperature dependence for relaxation by H₂O and D₂O is attributed to the fact that neither σ_c nor Γ are very sensitive to isotopic composition. As in the previous discussion, it appears that resonant V-V transfer within the complex plays a minor role. Assuming a Boltzmann distribution of rotational states in the complex, the population factors in Fig. 3 are again incompatible with the observed temperature dependence of $P_M(T)$. We note that in self-relaxation of water, V-R, T relaxation is more efficient than V-V transfer.¹⁷

A second unusual aspect of our data is the inverse isotope effect, with $P_{\text{D}_2\text{O}}/P_{\text{H}_2\text{O}} \approx 4$ over the entire temperature range. For nonresonant direct collisions one would expect H₂O to be the more efficient scattering partner because of its greater rotational velocity. On the other hand, for energy transfer within a complex, statistical factors are expected to be more important than dynamical ones. From information theory the prior microscopic rate constant is simply proportional to the density of product states.^{18,19} A direct count of energy levels gives for the ratio of density of states in the ground vibrational level

$$W_{\text{D}_2\text{O}}/W_{\text{H}_2\text{O}} = 4.528E^{0.0445}, \quad (11)$$

which is in fair agreement with the data. The mechanism we propose is vibrational predissociation of the ozone-water complex, with part of the energy defect absorbed by rotation of the water molecule.²⁰

It is interesting to compare the present results with the H₂O/D₂O isotope effects observed for other molecules. Various systems found in the literature are listed in Table II. Most of these systems have positive ($P_{\text{H}_2\text{O}} > P_{\text{D}_2\text{O}}$) isotope effects. For NO (Ref. 21) and CO (Ref. 22) the large positive effects are in agreement with the Sharma-Brau² theory. The case of HF (ν) is unclear. For HF ($\nu=1$), Hancock and Green observed $P_{\text{H}_2\text{O}} = P_{\text{D}_2\text{O}}$. They attribute the absence of an isotope effect to complex formation, but do not discuss the possible effect of the larger density of states of D₂O. For $\nu > 1$, Poole and Smith²³ observed a large isotope effect which they attribute to V-V, R resonant energy transfer. Their interpretation is supported by the positive isotope effect observed by Blauer *et al.*²⁴ for $\nu=1$ at high temperatures. However, note that the large anharmonicity of HF produces an energy defect of 206 cm⁻¹ for $\nu=1$, which would reduce the resonant contribution at room temperature. In the cases of Br(²P_{1/2}) (Ref. 25) and I(²P_{1/2}) (Refs. 26 and 27) the positive isotope effect may be attributed to a single quantum transfer for H₂O vs a double transfer for D₂O. For CO₂(001) (Ref. 28) the small inverse effect may be attributed to nearly 100% of the D₂O population being resonant, as compared with 60% for H₂O; however, the analysis is complicated by the different vibrational states involved for the two species. The normal isotope effect for CO₂(010) (Ref. 29) does not appear to be a resonant effect. Only V-R transitions

TABLE II. Relaxation of various molecules by H₂O and D₂O.

Molecule	Temperature range (°K)	M	P_M^a	Resonant product states	References
NO ($v=1$)	298	H ₂ O	0.22	H ₂ O (010)	21
		D ₂ O	2.42×10^{-3}		21
CO ($v=1$)	297	H ₂ O	7.8×10^{-4}	H ₂ O (010)	22
		D ₂ O	5.5×10^{-5}		22
HF ($v=1$)	294	H ₂ O	0.72	H ₂ O (001)	1
		D ₂ O	0.74	D ₂ O (110)	1
HF ($v=1$)	1500–2500	H ₂ O	0.14 ^b	H ₂ O (001) and (100)	24
		D ₂ O	0.04 ^b	D ₂ O (110)	24
HF ($2 \leq v \leq 7$)	298	H ₂ O	4.4 ^c	H ₂ O (001) and (100)	23
		H ₂ O	0.44 ^c	D ₂ O (110)	23
Br ($^2P_{1/2}$)	295	H ₂ O	0.16	H ₂ O (100)	25
		D ₂ O	0.049	D ₂ O (110)	25
I ($^2P_{1/2}$)	298	H ₂ O	1.57×10^{-2}	H ₂ O (101), (200)	26
	293	H ₂ O	5.9×10^{-3}	and (002)	27
	298	D ₂ O	2.8×10^{-4}	D ₂ O (201)	26
	293	D ₂ O	1.4×10^{-4}		27
CO ₂ (001)	298–580	H ₂ O	3.9×10^{-3}	CO ₂ (010) + H ₂ O (010)	28
		D ₂ O	7.8×10^{-3}	CO ₂ (000) + D ₂ O (020)	28
CO ₂ (010)	377–1211	H ₂ O	2.2×10^{-5d}		29
		D ₂ O	6.4×10^{-6d}		29
C ₃ (001)	295–453	H ₂ O	0.013	D ₂ O (010)	Present study
		D ₂ O	0.060	D ₂ O (010)	Present study

^aEvaluated at room temperature unless otherwise indicated.

^bEvaluated at 1500 °K.

^cEvaluated at $v=4$.

^d P_{H_2O} evaluated at 466 °K; P_{D_2O} at 477 °K.

are possible, and a second order calculation³⁰ yields a temperature dependence that is inconsistent with experiment. Finally, not unexpectedly, the dissociative quenching of Ar($^3P_{0,2}$) and Kr($^3P_{0,2}$) shows no isotope effect.³¹

In nearly every case considered (including O₃) the sign of the isotope effect can be predicted by examining the possible resonant transitions. In the present case we argue that this is due to the coincidence that the densities of both resonant and nonresonant states are four times larger for D₂O. The contribution of rotational velocity appears to be masked by other effects. In the case of CO₂(010), where resonances and complexes are not prominent, rotation may be responsible for the weak observed isotope effect. The faster self-relaxation of H₂O as compared to D₂O has also been attributed to rotational velocity.³² For many of these systems temperature dependent measurements would be helpful in clarifying the relaxation mechanism.

ACKNOWLEDGMENT

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¹⁵The fundamental frequencies of H₂O are $\nu_1=3652$, $\nu_2=1595$, and $\nu_3=3756$ cm⁻¹. For D₂O they are 2666, 1179, and 2789

- cm⁻¹, respectively.
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