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TEMPERATURE DEPENDENCE OF VIBRATIONAL RELAXATION IN GAS PHASE W--ETC(U)

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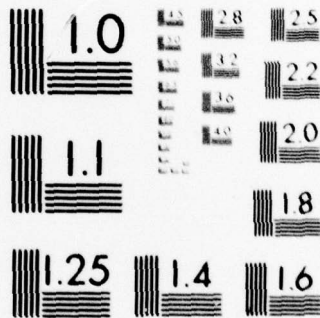
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TEMPERATURE DEPENDENCE OF VIBRATIONAL RELAXATION  
IN GAS PHASE WATER AND AMMONIA

by

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TEMPERATURE DEPENDENCE OF VIBRATIONAL RELAXATION IN GAS  
PHASE WATER AND AMMONIA

Floyd E. Hovis and C. Bradley Moore

Abstract

The vibrational relaxational rates of the coupled  $\nu_1$ ,  $\nu_3$  stretching level manifold and of the  $2\nu_2$  bending overtone level in  $\text{H}_2^{18}\text{O}$  has been studied from 250°K to 400°K using the method of laser excited vibrational fluorescence. The  $\nu_1$ ,  $\nu_3$  self deactivation rate constant goes from  $1.4 \mu\text{sec}^{-1} \text{Torr}^{-1}$  at 250°K to  $0.48 \mu\text{sec}^{-1} \text{Torr}^{-1}$  at 400°K. For  $2\nu_2$  it goes from  $4.5 \mu\text{sec}^{-1} \text{Torr}^{-1}$  to  $1.9 \mu\text{sec}^{-1} \text{Torr}^{-1}$ . The rate constants for deactivation by He and Ar are several hundred times slower and show a weak temperature dependence.

The V  $\rightarrow$  T, R relaxation rate for  $\text{NH}_3(\nu_2)$  has been studied from 198°K to 398°K by the same method as for water. The self deactivation rate constant decreases from  $2.4 \mu\text{sec}^{-1} \text{Torr}^{-1}$  at 198°K to  $0.65 \mu\text{sec}^{-1} \text{Torr}^{-1}$  at 398°K. The rate constants for He, Ar,  $\text{N}_2$ , and  $\text{O}_2$  are again much smaller and show the opposite temperature dependence.

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## I. VIBRATIONAL RELAXATION OF WATER

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The results of room temperature vibrational relaxational measurements for  $\text{H}_2^{18}\text{O}$  have been reported in a previously published paper.<sup>1</sup> To summarize, a tunable ir laser has been used to excite a variety of rotational states of the  $\nu_1$  and  $\nu_3$  stretching levels and fluorescence observed from  $\nu_3$ ,  $2\nu_2$ , and  $\nu_2$ . The total deactivation rate constants were determined for the coupled  $\nu_1$ ,  $\nu_3$  manifold and for  $2\nu_2$ . Limits were put on the  $\nu_2$  deactivation rate constant. There was not enough data to determine state-to-state  $V \rightarrow V$  and  $V \rightarrow T$ , R rate constants. However, relaxation rate and relative intensity measurements do show that the dominant, but not sole, relaxation channel is from the stretches to the bending overtone followed by successive  $V \rightarrow T$ , R transfers.

A higher energy Nd:YAG pumped optical parametric oscillator (OPO) has been used to do the temperature dependent studies. It put out 2 to 4 mJ/pulse at  $2.6 \mu$  with a  $0.15 \text{ cm}^{-1}$  bandwidth. All measurements were done exciting on the strongest  $\nu_3$  line at  $3839.8 \text{ cm}^{-1}$ .

Due to the higher laser power and larger bandwidth, scattered light was much more of a problem and it was not possible to extract rate constants from  $\nu_3$  emission. However both the  $\nu_1$ ,  $\nu_3$  and  $2\nu_2$  deactivation rate constants can be obtained from the time dependence of the  $2\nu_2$  fluorescence, with the rise giving the  $2\nu_2$  rate constant and the fall that for  $\nu_1$ ,  $\nu_3$ . This approach was used for the pure  $\text{H}_2^{18}\text{O}$  studies

and for those with mixtures of He and Ar.

The results for  $\nu_1$ ,  $\nu_3$  deactivation are given in Table I. The self deactivation rates show a clear decrease with increasing temperature, as do the probabilities. To establish the He and Ar deactivation rate constants, measurements were made at low mole fractions of  $\text{H}_2^{18}\text{O}$ . The rate constant for deactivation by the buffer gas was calculated from each measurement after correcting for self relaxation and then the results averaged. The He rate constant and probability are essentially constant with temperature over the range studied. The Ar rate constant shows a decrease at 250°K. It should be noted, however, that the 250°K and 293°K values nearly overlap within the estimated uncertainties. In light of this, plus the fact that the 293°K and 398°K rates are essentially the same, the decrease isn't considered as significant as it might appear at first glance.

The  $2\nu_2$  deactivation results are displayed in Table II. The self deactivation rate constants and probabilities show a definite decrease with increasing temperature. The rate constant for He increases slightly with increasing temperature. The Ar results, however, indicate a clear increase of rate constant with increasing temperature. These results are being written up for publication.

## II. VIBRATIONAL RELAXATION OF $\text{NH}_3$

By pumping  $\text{NH}_3(\nu_2)$ , the lowest vibrational level of

$\text{NH}_3$ , with a Tachisto  $\text{CO}_2$  TEA laser, its  $V \rightarrow T, R$  relaxation rate has been measured. All experiments were done in the presence of a buffer gas to enhance absorption of the laser and thus increase the signal to noise of the data. Initially a series of room temperature measurements were done using He, Ar,  $\text{O}_2$ , and  $\text{N}_2$  as the buffer gases. Different  $\text{CO}_2$  laser lines could be used to excite the  $aR(6, 0)$ ,  $sQ(5, 4)$ , or  $aR(1, 1)$  transitions of  $\text{NH}_3(v_2)$ . The same relaxation times were measured for all three rotational states. The results of the room temperature measurements have been recently published.<sup>2</sup>

After the room temperature studies were done, a variable temperature cell was built and the measurements were repeated at 198°K and 398°K. The results of these, plus the 293°K experiments, are summarized in Table III. As was seen in  $\text{H}_2^{18}\text{O}(v_1, v_3)$  and  $\text{H}_2^{18}\text{O}(2v_2)$ , the self deactivation rate constants show a significant decrease with increasing temperature. The buffer gases are much less efficient and show the opposite temperature dependence. It is interesting to note that He and Ar have nearly the same probabilities for deactivation. For a "normal"  $V \rightarrow T, R$  process one would expect He to be more efficient as a deactivator. These temperature dependent results are in the process of being written up for publication.



REFERENCES

1. J. Finzi, F.E. Hovis, V.N. Panfilov, P. Hess, and C.B. Moore, J. Chem. Phys. 67, 4053 (1977).
2. F.E. Hovis and C.B. Moore, J. Chem. Phys. 69, 4947 (1978).



TABLE I. Deactivation of  $\text{H}_2^{18}\text{O}(\nu_1, \nu_3)$  by M.

| M                         | T(°K)            | $k(\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})$ | $\sigma(\text{Å}^2)^b$ | $p^b$                |
|---------------------------|------------------|---------------------------------------------------------|------------------------|----------------------|
| $\text{H}_2^{18}\text{O}$ | 250              | $(3.5 \pm 0.35) \times 10^{-11}$                        | 4.9                    | 0.20                 |
|                           | 296 <sup>a</sup> | $(2.2 \pm 0.2) \times 10^{-11}$                         | 2.7                    | 0.11                 |
|                           | 400              | $(2.0 \pm 0.2) \times 10^{-11}$                         | 2.2                    | 0.088                |
| He                        | 250              | $(5.4 \pm 2.1) \times 10^{-14}$                         | $4.4 \times 10^{-3}$   | $2.2 \times 10^{-4}$ |
|                           | 296              | $(6.4 \pm 1.5) \times 10^{-14}$                         | $4.6 \times 10^{-3}$   | $2.3 \times 10^{-4}$ |
|                           | 400              | $(7.3 \pm 2.0) \times 10^{-14}$                         | $4.6 \times 10^{-3}$   | $2.3 \times 10^{-4}$ |
| Ar                        | 250              | $(2.8 \pm 1.0) \times 10^{-14}$                         | $4.5 \times 10^{-3}$   | $1.8 \times 10^{-4}$ |
|                           | 296 <sup>c</sup> | $(6.2 \pm 1.5) \times 10^{-14}$                         | $8.8 \times 10^{-3}$   | $3.5 \times 10^{-4}$ |
|                           | 400              | $(7.0 \pm 2.0) \times 10^{-14}$                         | $8.8 \times 10^{-3}$   | $3.5 \times 10^{-4}$ |
| $\text{N}_2$              | 293 <sup>a</sup> | $(4.6 \pm 1.2) \times 10^{-13}$                         | $6.4 \times 10^{-2}$   | $2.3 \times 10^{-3}$ |
| $\text{O}_2$              | 293 <sup>a</sup> | $(3.3 \pm 1.2) \times 10^{-13}$                         | $4.6 \times 10^{-2}$   | $1.8 \times 10^{-3}$ |

a. From reference 1.

b. Calculated using the molecular diameters  $d_{\text{H}_2\text{O}} = 2.8 \text{ Å}$ ,  $d_{\text{He}} = 2.24 \text{ Å}$ ,  $d_{\text{Ar}} = 2.86 \text{ Å}$ ,  $d_{\text{N}_2} = 3.15 \text{ Å}$ , and  $d_{\text{O}_2} = 2.93 \text{ Å}$ .

c. This value is smaller than that reported in reference 1 but these measurements were done under conditions where it could be more accurately measured.

TABLE II. Deactivation of  $\text{H}_2^{18}\text{O}(2\nu_2)$  by M.

| M                         | T(°K)            | $k(\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})$ | $\sigma(\text{Å}^2)^a$ | $p^a$                |
|---------------------------|------------------|---------------------------------------------------------|------------------------|----------------------|
| $\text{H}_2^{18}\text{O}$ | 250              | $(1.2 \pm 0.1) \times 10^{-10}$                         | 16                     | 0.65                 |
|                           | 296 <sup>b</sup> | $(9.1 \pm 1.2) \times 10^{-11}$                         | 12                     | 0.47                 |
|                           | 400              | $(7.8 \pm 0.8) \times 10^{-11}$                         | 8.6                    | 0.35                 |
| He                        | 250              | $(1.9 \pm 0.7) \times 10^{-13}$                         | $1.5 \times 10^{-2}$   | $7.6 \times 10^{-4}$ |
|                           | 296              | $(3.2 \pm 0.7) \times 10^{-13}$                         | $2.2 \times 10^{-2}$   | $1.1 \times 10^{-3}$ |
|                           | 400              | $(4.4 \pm 1.0) \times 10^{-13}$                         | $2.8 \times 10^{-2}$   | $1.4 \times 10^{-3}$ |
| Ar                        | 250              | $(2.0 \pm 0.4) \times 10^{-13}$                         | $3.0 \times 10^{-2}$   | $1.2 \times 10^{-3}$ |
|                           | 296              | $(3.2 \pm 0.7) \times 10^{-13}$                         | $4.8 \times 10^{-2}$   | $1.9 \times 10^{-3}$ |
|                           | 400              | $(7.6 \pm 1.4) \times 10^{-13}$                         | $9.3 \times 10^{-2}$   | $3.7 \times 10^{-3}$ |

a. Calculated using the molecular diameters  $d_{\text{H}_2\text{O}} = 2.80 \text{ Å}$ ,  $d_{\text{He}} = 2.24 \text{ Å}$ , and  $d_{\text{Ar}} = 2.86 \text{ Å}$ .

b. From reference 1.

TABLE III. Deactivation of  $\text{NH}_3(\nu_2)$  by M.

| M             | T(°K)            | $k(\text{cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1})$ | $\sigma(\text{Å}^2)^b$ | $p^b$                |
|---------------|------------------|---------------------------------------------------------|------------------------|----------------------|
| $\text{NH}_3$ | 198              | $(4.9 \pm 0.7) \times 10^{-11}$                         | 6.9                    | 0.22                 |
|               | 293 <sup>a</sup> | $(3.8 \pm 0.4) \times 10^{-11}$                         | 4.4                    | 0.14                 |
|               | 398              | $(2.7 \pm 0.4) \times 10^{-11}$                         | 2.7                    | 0.085                |
| He            | 198              | $(1.1 \pm 0.2) \times 10^{-13}$                         | 0.010                  | $4.4 \times 10^{-4}$ |
|               | 293 <sup>a</sup> | $(2.8 \pm 0.3) \times 10^{-13}$                         | 0.020                  | $8.8 \times 10^{-4}$ |
|               | 398              | $(4.1 \pm 0.3) \times 10^{-13}$                         | 0.025                  | $11 \times 10^{-4}$  |
| Ar            | 198              | $(7.3 \pm 1.7) \times 10^{-14}$                         | 0.012                  | $4.2 \times 10^{-4}$ |
|               | 293 <sup>a</sup> | $(1.8 \pm 0.2) \times 10^{-13}$                         | 0.025                  | $8.7 \times 10^{-4}$ |
|               | 398              | $(3.6 \pm 0.3) \times 10^{-13}$                         | 0.043                  | $15 \times 10^{-4}$  |
| $\text{N}_2$  | 198              | $(1.9 \pm 0.3) \times 10^{-13}$                         | 0.030                  | $9.5 \times 10^{-4}$ |
|               | 293 <sup>a</sup> | $(3.6 \pm 0.3) \times 10^{-13}$                         | 0.047                  | $15 \times 10^{-4}$  |
|               | 398              | $(4.5 \pm 0.4) \times 10^{-13}$                         | 0.050                  | $16 \times 10^{-4}$  |
| $\text{O}_2$  | 198              | $(1.5 \pm 0.25) \times 10^{-13}$                        | 0.025                  | $8.6 \times 10^{-4}$ |
|               | 293 <sup>a</sup> | $(4.2 \pm 0.4) \times 10^{-13}$                         | 0.056                  | $19 \times 10^{-4}$  |
|               | 398              | $(6.1 \pm 0.5) \times 10^{-13}$                         | 0.070                  | $24 \times 10^{-4}$  |

a. 293°K results taken from reference 2.

b. Calculated using the molecular diameters  $d_{\text{NH}_3} = 3.17 \text{ Å}$ ,  
 $d_{\text{He}} = 2.24 \text{ Å}$ ,  $d_{\text{Ar}} = 2.86 \text{ Å}$ ,  $d_{\text{N}_2} = 3.15 \text{ Å}$ , and  $d_{\text{O}_2} = 2.93 \text{ Å}$ .



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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Vibrational relaxation measurements are reported on H<sub>2</sub> (180  $\bar{\nu}$ , 8 and 272 from 250°K to 400°K for pure water and for mixtures with He and Ar. The results of vibrational relaxation measurements of NH<sub>3</sub> (16) in mixtures of He, Ar, N<sub>2</sub>, and O<sub>2</sub> are reported for the temperature range 198°K to 398°K.

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