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Rate Constants for the Reaction of $Ar^+(^2P_{3/2})$ With N_2 as a Function of N_2 Vibrational Temperature and Energy Level

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Rate constants for the reaction of $Ar^+(^2P_{3/2})$ with N_2 as a function of N_2 vibrational temperature and energy level

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Rate constants have been measured for the reaction of $Ar^+(^2P_{3/2})$ with N_2 as a function of N_2 vibrational temperature for a rotational and translational temperature of 300 K. The rate constants increase from a value of 1.2×10^{-11} $cm^3\,s^{-1}$ at a N_2 vibrational temperature of 300 K to 2.0×10^{-10} $cm^3\,s^{-1}$ at a N_2 vibrational temperature of 4700 K. The data are used to derive rate constants for specific vibrational levels. The rates constants for $v=0$–3 are 1.2×10^{-11}, 3.0×10^{-10}, 7.6×10^{-10}, and 7.6×10^{-10} $cm^3\,s^{-1}$, respectively. Additionally, the data suggest that the rate constant for $v>3$ drops from the $v=3$ value, although this is less certain. The increase in the rate constants with increasing v is postulated to arise from the $N_2(v)\rightarrow N_2^+(v+1)$ channel becoming less endothermic with increasing v and therefore closer to being resonant. Vibrational energy is found to be more effective at promoting this reaction than are translational or rotational energy.

INTRODUCTION

The charge transfer reaction of Ar^+ with N_2,

$$Ar^+ + N_2 \rightarrow N_2^+ + Ar \qquad (1)$$

is certainly one of the most studied reactions in all of gas phase chemistry. Numerous experimental and theoretical studies have examined this reaction and the reverse reaction in detail. The experimental studies have been summarized by Ng[1] and Guyon *et al.*,[2] and the theoretical studies have been summarized by Gislason *et al.*[3] Most types of energy dependencies for this reaction have been studied. One of the only dependencies that has not been previously examined is the dependence on the vibrational level of N_2. We have shown previously that rotational and translational energies are equally effective at driving this reaction[4,5] and have been interested in examining whether vibrational energy would also be equally effective. In this paper, we report measurements of the vibrational temperature dependence of the rate constants for reaction (1) and use this dependence to derive information on the rate constants for individual vibrational levels.

EXPERIMENT

The measurements were made using the Phillips Laboratory variable temperature-selected ion flow drift tube apparatus (VT-SIFDT). The apparatus has been described in detail,[6,7] and we will discuss here only those aspects that are relevant to the present study. Ar^+ ions were generated in a relatively high pressure ion source and injected into a helium buffer. In a previous paper[4] it has been shown that Ar^+ ions produced in a high pressure ion source are in the ground $^2P_{3/2}$ state. In the present experiment, no curvature was seen in semilogarithmic plots of Ar^+ signal decay vs N_2 flow rate, lending support to the conclusion that essentially only ground state $Ar^+(^2P_{3/2})$ is present in the reaction zone of our experiment when the discharge is off. Formation of $Ar^+(^2P_{1/2})$ by energy transfer from $N_2(v>0)$ could in principle produce $Ar^+(^2P_{1/2})$, which would complicate the interpretation of our results. The rate constant for that process is unknown, but the reaction would have to be very efficient to influence the present results. In addition, it is known that deexcitation of $Ar^+(^2P_{1/2})$ by N_2 occurs[8] and since under all conditions $N_2(v=0)$ is dominant over $N_2(v>0)$, any $Ar^+(^2P_{1/2})$ produced could also be quenched before reaction. A final consideration is that the rate constants derived for $N_2(v=2,3)$ charge transfer are equal to the collisional value (see below) and therefore preclude any significant energy transfer process for these states. For these reasons, we feel that while we cannot exclude the possibility of $Ar^+(^2P_{1/2})$ formation by $N_2(v)$, it is unlikely and assumed not to be of consequence.

N_2 vibrational excitation was produced by flowing a mixture of approximately 6% N_2 in He through a microwave discharge. The microwave inlet consisted of two glass tubes connected by a Teflon right angle elbow. The discharge was upstream of the right angle bend. The amount of vibrational excitation was varied in two ways: (1) the power to the microwave was varied from 5–80 W; (2) the distance from the discharge to the right angle was varied.

The present apparatus does not include diagnostics to measure the N_2 vibrational temperature directly. Rather, we used the reaction of O^+ with N_2 as a calibration to derive the N_2 vibrational temperature. This reaction was studied at the National Oceanic and Atmospheric Administration (NOAA) laboratories and was found to be very sensitive to the N_2 vibrational temperature.[9,10] The NOAA workers reported rate constants for the reaction of O^+ with vibrationally excited N_2 as a function of N_2 vibrational temperature. The present calibration procedure is as follows: O^+ was injected into the flow tube and the signal measured $[(O^+)_0]$. N_2 was added with the discharge off and the O^+ signal measured $[(O^+)_{off}]$. The discharge was then turned on and the O^+ signal measured $[(O^+)_{on}]$. The logarithm of the ratio of the O^+ signal with no N_2 added to that with N_2 flowing is related to the rate constant for O^+ reacting with N_2. The ratio of rate constants for N_2 at a vibrational temperature T to that for 300 K N_2 is then given by

$$\frac{k(T)}{k(300)}=\frac{\ln[(O^+)_0/(O^+)_{\rm on}]}{\ln[(O^+)_0/(O^+)_{\rm off}]}. \tag{2}$$

All other parameters that normally go into deriving rate constants cancel. The rate constant for the reaction of O^+ with vibrationally excited N_2 $[k(T)]$ is derived by using the value for $k(300)$ measured in the NOAA experiment. This is preferred to using a rate constant measured in our apparatus to avoid introducing a systematic error since the NOAA data are used as the calibration of N_2 vibrational temperature. In any case, the value measured in our experiment is only about 20% larger than the NOAA value and therefore well within the error limits of about 25% for each experiment. The N_2 vibrational temperature is then determined by comparing $k(T)$ with the graph of rate constant vs N_2 vibrational temperature given in the NOAA article. It is estimated that the derived temperature is accurate within 100 K.

With the discharge still on, the injected ion species is then changed from O^+ to Ar^+. The discharge is then turned off, and finally the N_2 flow is turned off. An equation similar to that given above is then used to derive the ratio of the Ar^+ rate constant at the vibrational temperature T compared with that for a vibrational temperature of 300 K. The rate constant for the vibrationally hot N_2 is derived by using the present measured 300 K rate constant of 1.2×10^{-11} $cm^3\,s^{-1}$.

As an alternative to the above procedure, repeat measurements involving the same ion were made to ensure that the discharge was stable over the time period of the measurements. No measurable drift was found. It should be noted that any N atoms produced in the discharge should not interfere with the present measurements since neither O^+ nor Ar^+ reacts with N.

RESULTS AND DISCUSSION

Figure 1 shows a plot of the rate constants for the charge transfer of Ar^+ with N_2 as a function of the N_2 vibrational temperature. The rate constant is found to increase from 1.2×10^{-11} $cm^3\,s^{-1}$ at 300 K to a value of 2.0×10^{-10} $cm^3\,s^{-1}$ at 4700 K. It is clear from Fig. 1 that vibrational energy is very effective at promoting this reaction.

Previously, we have shown that rotational energy and translational energy have the same effect on the rate constant.[4,5] This was shown by plotting the rate constants for reaction (1) as a function of total energy and showing that all the data, measured as a function of translational energy (by varying an applied electric drift field) at several temperatures, fit on a single curve. Figure 2 shows the present data and our previous data as a function of average total energy. Our previous data correspond to the sums of average translational and rotational energies only, since no appreciable populations of vibrationally excited N_2 were present. The present results include the average vibrational energy assuming that the vibrations are populated in a Boltzmann distribution. The NOAA workers, using an apparatus similar to the present one, concluded that the populations could be described by a Boltzmann distribution.[9,10] The present rate constants are significantly larger than those for which N_2 is unexcited. This shows that vibrational excitation is significantly more effective in promoting this reaction than is translational or rotational energy. Spin excitation is also known not to be equivalent to translational or rotational energy in promoting this reaction.[8,11,12]

The present data cover a wide range of vibrational temperatures and can be used to derive rate constants for the first several vibrational levels. The rate constant for $v=0$ is given simply as the 300 K rate constant since there is essentially no vibrational excitation of N_2 at 300 K. For higher levels, the measured rate constant k is the sum of the rate constants for each vibrational level multiplied by the population of that level $k=\Sigma[k(v)*\mathrm{pop}(v)]$.

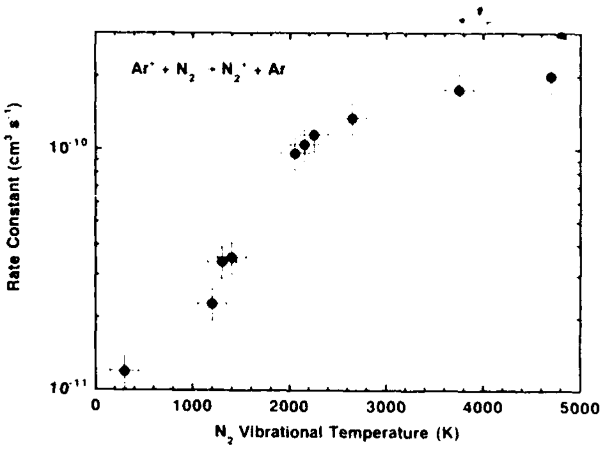

FIG. 1. Rate constants for the reaction of $Ar^+(^2P_{3/2})$ with N_2 as a function of N_2 vibrational temperature.

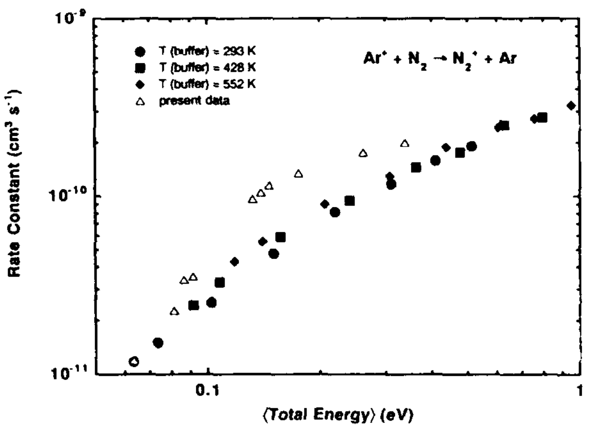

FIG. 2. Rate constants for the reaction of $Ar^+(^2P_{3/2})$ with N_2 as a function of total energy. Included are the present results and those of Viggiano *et al.* (Ref. 4) at three temperatures.

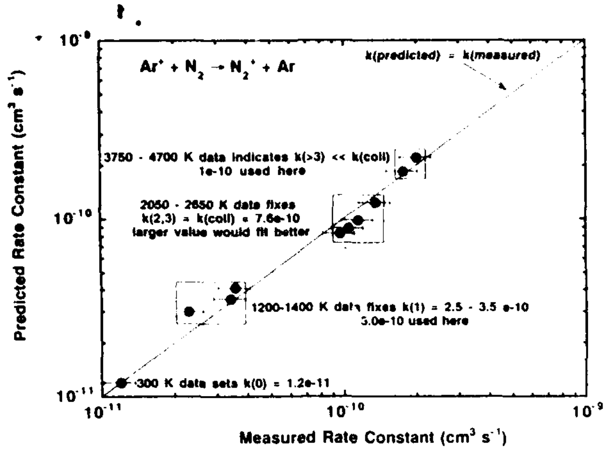

FIG. 3. The measured rate constants for the reaction of $Ar^+(^2P_{3/2})$ with N_2 for various N_2 vibrational temperatures vs the predicted rate constants calculated using derived state specific rate constants for various N_2 vibrational levels.

TABLE I. Rate constants for individual vibrational levels of N_2 and the energy gaps for the near resonant process. The error limit for $v=0$ is the standard 25% error. Error limits for other levels are estimates of the errors in the fitting procedure and assume that the temperature is derived accurately.

N_2 vibrational level	Rate constant ($cm^3\ s^{-1}$)	Energy gap reaction (4) (eV)[a]
0	$1.2 \pm 0.3 \times 10^{-11}$	+0.090
1	$3 \pm 0.5 \times 10^{-10}$	+0.067
2	$7.6 \pm 1 \times 10^{-10}$	+0.043
3	$7.6 \pm 1.5 \times 10^{-10}$	+0.020
>3	$<7.6 \times 10^{-10}$	−0.006 ($v=4$)

[a] Reference 18.

The rate constant for $v=1$ can be derived most readily from the data in the 1200–1400 K range. In this vibrational temperature range, essentially all N_2 is in either the $v=0$ or $v=1$ level; the $v=2$ population is less than 9% of the $v=1$ population. Therefore, only if the $v=2$ rate constant is much greater than the $v=1$ rate constant will the overall rate constant be affected substantially by the $v=2$ (and higher) level. This gives a relatively good estimate of the $v=1$ rate constant as $2.5–3.5 \times 10^{-10}\ cm^3\ s^{-1}$. The largest rate constant that is possible is the collisional value[13,14] of $7.6 \times 10^{-10}\ cm^3\ s^{-1}$, and therefore the assumption that the higher levels do not affect the determination of the $v=1$ rate constant is good. Continuing this procedure on the data in the 2050–2650 K range yields an estimate of the $v=2$ and 3 rate constants. The data are only fit reasonably well if both of these rate constants are set equal to the Langevin value of $7.6 \times 10^{-10}\ cm^3\ s^{-1}$. A slightly higher value would give a slightly better fit. Higher values would imply a harpoon mechanism at long range for the charge transfer. For simplicity, a rate constant larger than the Langevin value is not considered here. Finally, information on levels higher than $v=3$ is obtained from the data in the 3750–4700 K range. At 3750 and 4700 K, 3% and 6% of the molecules, respectively, are in vibrational levels higher than $v=3$. Assuming rate constants for these higher levels equal to the collisional value yields a poorer fit to the data than do lower values, but only slightly. Thus, the data suggest, but do not prove, that the rate constants for these levels are smaller than the Langevin value derived for $v=2$ and 3. The data do not indicate how much smaller they may be. Changing the rate constant for $v>3$ from zero to the Langevin value changes the predicted rate constant by less than 20%.

Figure 3 shows a plot of the predicted rate constants (from the above analysis) vs the measured rate constants. The straight line represents what would be a perfect prediction. The parameters used in the fit are given on the graph. All of the rate constants involved in this comparison were varied to obtain the best fit. Increasing the $v=1$ rate constant by more than 20% gave a significantly poorer fit to the low vibrational temperature points, although the midrange points benefited from a slightly larger rate constant. Lowering the $v=1$ rate constant gave a poorer fit to the midrange data. Any lower values of the $v=2$ and 3 rate constants gave a worse fit to the midrange temperature data. As noted above, a larger value for these rate constants is limited by the collision rate constant and also resulted in a worse fit to the high temperature data. Increasing the $v>3$ rate constants resulted mainly in a larger rate constant for the highest temperature point and therefore in a worse fit. However, this sensitivity is slight and is not nearly as convincing as that in the derivation of the other state specific rate constants. The rate constants derived in this manner are also consistent with the fact that vibrational energy promotes this reaction more readily than does translational or rotational energy.

For N_2 in the ground vibrational level, the reaction with Ar^+ is known to proceed mainly (>90% at 300 K) by the near resonant endothermic channel[15,16]

$$Ar^+(^2P_{3/2}) + N_2(v=0) \rightarrow N_2^+(v=1) + Ar - 0.09\ \text{eV} \quad (3)$$

rather than by the exothermic channel producing $v=0$ ($\Delta H = -0.0179$ eV).[17] The vibrational spacing for N_2^+ vibrational levels is less than that for N_2 (Ref. 18) and therefore the energy difference for the near resonant processes

$$Ar^+(^2P_{3/2}) + N_2(v=n) \rightarrow N_2^+(v=n+1) + Ar \quad (4)$$

becomes less as v increases. Table I lists the rate constants derived for the various N_2 vibrational levels as well as the energy differences (gaps) for the near resonant process (4).

There is a strong correlation between the size of the energy gap and the rate constants for $v=0–3$. The "endothermicity" for $v=2$ and 3 is less than the sum of the average translational and rotational energies (0.063 eV) available to drive the reaction. The fact that the $v=2$ and 3 reactions proceed at or near the collisional rate while some of the reactants will not have enough energy to overcome the slight endothermicity indicates that at least some of the reaction must proceed by other channels. Thus, while the above analysis suggests that the mechanism for the higher vibrational levels is similar to that for the $v=0$

channel, namely resonant charge transfer, the data also suggest that an appreciable fraction of the reaction proceeds by more exothermic channels.

The result that the rate constants for vibrational levels higher than $v=3$ are less than collisional contradicts the above analysis since the $(v \rightarrow v+1)$ channel becomes "exothermic." This may indicate that the dynamics are more subtle than described above or alternatively may indicate that it is not possible to derive rate constants for the levels higher than $v=3$.

A recent study by Tosi[19] may shed some light on our results. He studied the total cross section for the reaction of Ar^+ with $N_2(v=0)$ as a function of energy in a guided ion crossed beam apparatus. His measurements have good energy resolution, allowing for observations of thresholds for production of vibrationally excited states. The cross section increases up to the threshold for $v=4$ after which it decreases. Our results also indicate a reduction of the rate constant when the production of $N_2^+(v=4)$ is likely, i.e., from $N_2(v=3)$.

There has been one theoretical study of the reactivity of vibrationally excited N_2 with $Ar^+(^2P_{3/2})$.[20] Cross sections for state-to-state reactivity were calculated for the first four levels each of N_2 and N_2^+. The model used a number of simplifying assumptions that pertain to higher energy collisions, and therefore the predictions do not apply to the present situation. The lowest collision energy used in the predictions was 1.2 eV, and a direct comparison is not possible. Nevertheless, it is interesting to compare the theoretical results with the present results. In agreement with the above analysis, the theoretical results indicate that the reaction proceeds mainly through reaction (4). This process accounts for 100%, 89%, 59%, and 73% of the reactivity for $v=0$, 1, 2, and 3, respectively. In contrast to our results, the theory predicts total cross sections that initially decrease with increasing N_2 vibrational level and then increase again for $v=3$.

CONCLUSIONS

In summary, we have measured rate constants for the reaction of $Ar^+(^2P_{3/2})$ with N_2 as a function of the N_2 vibrational temperature. From these data, we are able to derive rate constants for the specific N_2 vibrational levels 0–3 and possibly for a lumped "state" $v>3$. The derivation of vibrationally state specific rate constants for a relatively large number of levels is possible in this system for several reasons (1) the vibrational temperature was varied over a large range; (2) the vibrational spacings are large in N_2. This large spacing then allows one to separate the data into ranges in which only one rate constant is unknown and keeps the number of levels populated small; (3) the rate constants increase with energy. This is important since the populations of the higher levels decrease substantially, even at high energy. Therefore, the contribution to the overall rate constants from these higher lying levels is only important if the rate constant for high lying levels is larger than that for lower lying levels. Even at a temperature of 4700 K, $v=0$ accounts for over half of all molecules, and therefore if the $v=0$ rate constant were large, it would dominate the overall rate constant. It is the combination of all of the above factors that allowed us to derive the state specific rate constants.

A large dependence on the vibrational level is found. A value of almost 30 is derived for the ratio of the $v=1$ rate constant to that for $v=0$. A factor of 3 is found for the ratio of the $v=2$ rate constant to that for $v=1$. The rate constant for $v=2$ is equal to the collisional value. The $v=3$ rate constant is found to be the same as $v=2$. There is a suggestion in the data that the $v>3$ rate constant drops from the collisional value, but this is less certain.

The trends are consistent with the N_2^+ product being produced mainly in a vibrational level one higher than that of the N_2 reactant. This is known to occur for N_2^+ produced in $v=1$ from $N_2(v=0)$ and is a slightly endothermic resonant process. The endothermicity is less for each successive vibrational level since the spacing in N_2^+ is slightly less than that in N_2. The declining endothermicity is postulated to be, at least in part, the reason for the dramatically increasing rate constants with vibrational level.

While there is an increasing amount of information on state selected ion-molecule reactions,[21] little is known about the effect of neutral vibrations. The situation arises mainly from the ability to state select the ion by various photoionization methods, especially multiphoton ionization. By contrast, it is difficult to state select neutral molecules. Techniques such as stimulated emission pumping can populate specific vibrational levels, but leave a large fraction of molecules in both the $v=0$ state and a high level (electronic) state used in the pumping process. Therefore, the less state specific techniques such as described in this paper complement the more detailed information derived from laser experiments.

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