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A.A. Viggiano*, Robert A. Morris#, John F. Paulson

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Rotational temperature dependences of gas phase ion–molecule reactions

A. A. Viggiano,[a] Robert A. Morris,[b] and John F. Paulson
Air Force Geophysics Laboratory, Ionospheric Interactions Branch, Hanscom Air Force Base, Massachusetts 01731-5000

A technique for measuring the rotational temperature dependences of gas phase ion–molecule rate constants is presented. The technique involves measuring the kinetic energy dependences of the rate constants at several temperatures in a variable temperature selected ion flow drift tube. For a monatomic ion, comparing the rate constants at the same center of mass kinetic energy at different temperatures yields the dependence of the rate constant on the internal temperature of the reactant neutral. For neutrals in which the vibrational modes are inactive at the temperatures of the experiment, the internal energy dependence is the rotational temperature dependence. Two examples are presented here, one in which rotational energy significantly influences the rate constants, approximately $T^{-0.5}$, and one in which it does not. Implications for past drift tube experiments are discussed.

INTRODUCTION

Gas phase ion–molecule reactions have been extensively studied and over 10 000 rate constants for these reactions have been measured.[1] The work has included information on how temperature, ion kinetic energy, and vibrational state affect the reaction rate constant. However, little if any information is available on the dependence of rates of reaction on rotational energy. In fact, in discussions of the effects of internal energy on ion–molecule reactions, rotational effects are generally ignored[2] except in association reactions.[3-5] Likewise, little information is available on the effect of rotational energy on the rates of neutral reactions.[6]

We present here a technique using a variable temperature flow drift tube to study the effect of rotational temperature of the reactant neutral on gas phase ion–molecule reactions. This technique is useful only for reactions involving monatomic ions and neutrals with vibrational energies in excess of thermal energies. In the present paper we will discuss the technique and show two examples, one in which rotational energy has little effect on the rate constant and one in which the rate constant does change significantly.

EXPERIMENTAL

The measurements are made in a variable temperature selected ion flow drift tube (VT-SIFDT). An apparatus similar to ours has been described in detail by Smith and Adams.[7] Briefly, ions are created in an external ion source, mass selected, and injected into a flow tube through a Venturi inlet. The ions are carried down the flow tube by a fast flow of a buffer gas, usually helium. The flow tube is 1 m long, the last 60 cm incorporating a drift tube consisting of 60 guard rings. A potential is applied to the drift tube and distributed uniformly over the rings through a series of resistors. This allows the laboratory energy of the ions to be varied from thermal to approximately 2 eV (in favorable cases). The drift tube is terminated by a truncated nose cone with a 0.2

mm hole through which the ions are sampled. The ions are then mass analyzed by a quadrupole mass filter and detected by a Channeltron electron multiplier.

Rate constants are measured by monitoring the decrease in the primary ion intensity upon addition of the reactant neutral at one of several inlet positions in the drift tube. This decay, together with the measurements of temperature, pressure, and ion residence time, allow a determination of the reaction rate constant.

The ion residence time, and therefore the ion velocity in the drift region, is measured by pulsing two different drift rings with a retarding pulse and measuring, with the mass spectrometer, the arrival times of the perturbations in the ion signal. Pulsing two rings reduces systematic errors resulting from the pulsing method and also accounts for the time spent in the analyzer region. The drift velocity of the ion is the velocity of the ion with the field on minus the velocity of the ion with the field off. The latter quantity is the velocity due to the flow of the carrier gas. Both the zero field velocity and the drift velocity are measured during the course of a set of experiments. The ion kinetic energy is calculated using the Wannier expression[8] (see below) using this measured drift velocity.

Temperature in the flow tube can be varied over the range 85 to 550 K. This is accomplished by a series of heat exchangers in contact with the tube. Liquid nitrogen or cooled methanol is used for cooling and hot oil for heating. The temperature uniformity as measured by six platinum resistance thermometers along the tube is within 3%. The laboratory ion kinetic energy can be varied from thermal energy to approximately 2 eV.

RESULTS AND DISCUSSION

To interpret the results of a study of ion–molecule rate constants as a function of temperature and electric field, four energy distributions or temperatures must be known. The four temperatures/energies are (1) the temperature of the bath gas and thus of the reactant neutral, (2) the center of mass kinetic energy between the ion and reactant neutral,

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(3) the rotational energy of the ion, and (4) the vibrational energy of the ion.

The temperature of the bath gas controls the temperature of the reactant neutral and influences the ion energy through the thermal term in the Wannier expression[8]

$$KE_{ion} = \tfrac{1}{2} m v_d^2 + \tfrac{1}{2} M_b v_d^2 + \tfrac{3}{2} kT, \qquad (1)$$

where m is the mass of the reactant ion, M_b is the mass of the buffer, and v_d is the drift velocity. The ions have three separate energy distributions, translational, rotational, and vibrational. It has been found[2] that the average translational energy can be calculated from the drift velocity using the Wannier expression.[8] It has been predicted[9] and confirmed experimentally[10] that the rotational energy of the ion can be represented by the center of mass kinetic energy of the ion with respect to the bath gas. For an infinitely long drift tube this equality is also true for vibrational energy.[9] However, in practice the vibrational energy of the ion is usually lower than predicted, especially in the commonly used buffer gas helium.[11,12]

The fact that there are four separate temperature/energy distributions in a drift tube makes analysis of the data quite complicated. Nevertheless, there are abundant data on the effect of vibrational energy in drift tubes. Qualitative information has been derived by comparing rate constants obtained in different buffer gases.[13] This procedure is effective because more vibrational and rotational excitation of the ion occurs in heavy buffers than in light buffers at the same center of mass kinetic energy with respect to the reactants. In these studies rotational excitation was either ignored or deemed irrelevant. More recent studies[14] involving other techniques have resulted in quantitative information on reactivity as a function of vibrational quanta.

The complicated situation in a drift tube is greatly simplified when a monatomic ion is used. The electric field then changes only the ion translational energy and therefore the center of mass collision energy. The pure kinetic energy dependence of the reaction rate constant at a particular temperature of the reactant neutral is then readily obtained. Interpretation of the results is still not straightforward since only the mean relative energy is known and not the distribution function. The distribution at a particular mean energy can vary significantly in different buffers, yielding experimental rate constants that depend on buffer as well as mean kinetic energy.[15] This is especially true for reactions that depend strongly on the high energy tail of the distribution, since it is this part of the distribution that is most affected by a change of buffer.[15]

Fortuitously, the distribution function in a helium buffer is sufficiently close to Maxwellian that the kinetic energy dependence of the rate constants measured in a helium buffer does not differ greatly from that which would be found for a Maxwellian distribution.[15–18] For example, in the reaction of Si$^+$ with O$_2$, a correction of less than 10% is necessary to convert the rate constant measured in a drift tube with a He buffer to that which would be found for a Maxwellian distribution.[16] This is the case even though the rate constant varies by a factor of 30 (and is therefore very sensitive to changes in the distribution function) over the

energy range from thermal to 1 eV at 300 K. For the reaction of N$^+$ + NO, where there is only a slight energy dependence, less than a 2% correction is needed.[17] The energy dependences in the present study are small, and therefore one would expect small corrections to be needed.

The simple situation of a monatomic ion drifting in a He buffer (no internal modes of the ion and an approximately Maxwellian energy distribution) leads to the interesting possibility of determining the dependence of the rate constant upon the rotational temperature of the reactant neutral from a measurement of the kinetic energy dependence of the rate constant at several temperatures. This dependence upon rotational temperature of the reactant neutral is obtained simply by comparing data at a particular kinetic energy at several different temperatures. This procedure assumes that the vibrational modes of the neutral are sufficiently high in energy that they are not excited at the temperatures used in the experiments. In cases where the vibrational modes are active, the measured temperature dependence would reflect the dependence on both rotational and vibrational energy.

Two contrasting examples are given below. Figure 1 shows the dependence of the rate constant upon kinetic energy for the reaction of O$^-$ with N$_2$O at several temperatures. The rate constants at various temperatures fall on one curve within experimental error. Only slight differences ($\leqslant 15\%$) are seen at different temperatures indicating that this reaction is not very sensitive to the internal energy of N$_2$O. The slight differences can either represent a small internal energy dependence or may possibly be due to the small difference in the velocity distributions that can be expected.

In contrast to the case given above, the rate constants for the reaction of O$^-$ with CH$_4$ show a significant dependence on the rotational temperature of the CH$_4$. Figure 2 shows the rate constants for this reaction plotted as a function of kinetic energy at several temperatures. Unlike the case for the O$^-$ + N$_2$O reaction, separate curves are required to represent the kinetic energy dependence at each temperature.

At the highest temperatures there is some vibrational excitation of the N$_2$O and CH$_4$ in these experiments. The fraction of N$_2$O molecules with vibrational excitation is 0.33, 0.12, and 0.03 at 450, 300, and 205 K, respectively.[19] Most of the excitation is in the degenerate bending modes. For CH$_4$, the fractions are 0.07 and 0.006 at 500 and 295 K, respectively, and are negligibly small at lower temperatures.[19] Only if the fractional amount of vibrational excitation is on the or-
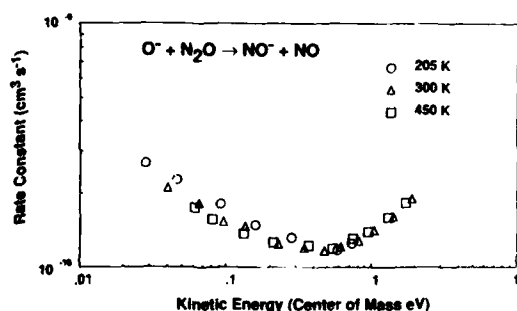

FIG. 1. Rate constants for the reaction of O$^-$ + N$_2$O vs center of mass kinetic energy at several temperatures.
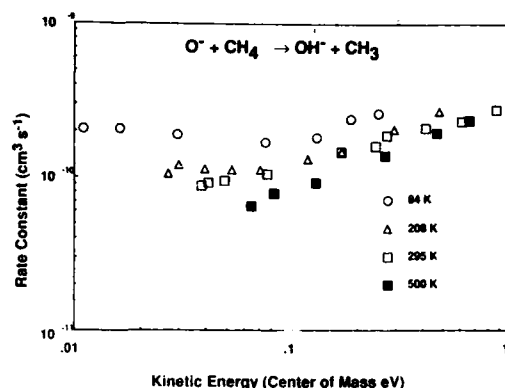
FIG. 2. Rate constants for the reaction of $O^- + CH_4$ vs center of mass kinetic energy at several temperatures.

der of or larger than the reaction efficiency can vibrational excitation have a pronounced effect on the reaction rate. Then the rate constant for the vibrationally excited population can compete with that for the ground vibrational state.

The reaction of O^- with N_2O proceeds at approximately 10%–25% of the collision rate. These values are on the same order as the level of vibrational excitation at the higher temperatures. The fact that the rate constant does not vary with the temperature of the N_2O then indicates that neither rotational excitation nor the bending mode vibration affects the rate constant significantly. There is, however, a slight possibility that the two types of excitation could compensate for each other.

For CH_4, the reaction proceeds at 5%–15% of the collision rate. Except at 500 K, this is significantly higher than the fraction of CH_4 that is vibrationally excited. Therefore, the difference between the kinetic energy curves is due to rotational effects except possibly at 500 K.

Comparing the rate constants for $O^- + CH_4$ at a particular kinetic energy at several temperatures yields the rotational temperature dependence. Figure 3 shows such comparisons at 0.06 and 0.25 eV, the lowest and highest kinetic energies for which there are data at all temperatures studied. The temperature dependence of the rate constant for this
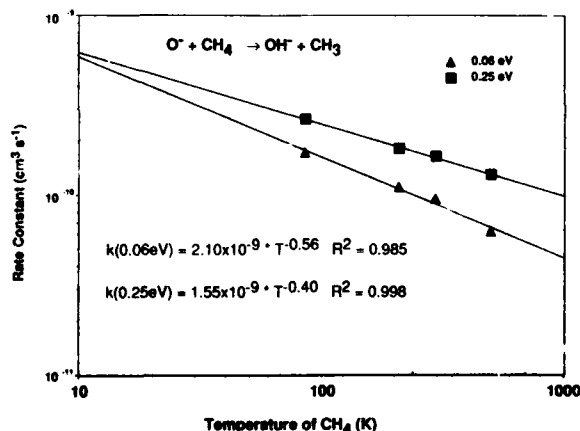
reaction was found to be $T^{-0.56}$ at 0.06 eV and $T^{-0.40}$ at 0.25 eV. The rate constants vary by a factor of 2.7 and 2.0 over the temperature range 85 to 500 K at 0.06 and 0.25 eV, respectively. These changes are considerably larger than what can be attributed to the velocity distribution differences in a helium buffer, which we expect to be less than 10%.[15–17] The fact that the data at 500 K are in line with the lower temperature data indicates that the 7% of the CH_4 that is vibrationally excited at this temperature does not strongly affect the rate constant.

Figure 4 shows the rotational distributions of CH_4 at four different temperatures.[19] At the lowest temperature, 84 K, the distribution shows a peak at J equal to 3 with a peak width of 3 levels at half-maximum. The 500 K distribution has a broad peak at J equal to 6 and has a width of 9 J levels. Combining these results with the data shown in Fig. 3 leads to the conclusion that increasing the rotational energy level decreases the rate constant for this reaction. The causes of the rotational energy effect on the rate constants are currently under investigation theoretically and will be discussed in a later paper.

Similarly large rotational temperature dependences have been found in our laboratory for other reactions, including the reactions of F^- with CH_3Br and CH_3I, as well as the reactions of O^- with CD_4 and CH_2D_2.[20] In the latter cases, the magnitude of the rate constants and their dependence on kinetic energy changes dramatically with isotope substitution although the dependences on rotational temperature do not. Of further interest is that the branching ratio for the CH_2D_2 reaction depends only on kinetic energy and does not depend on the rotational energy (temperature). In all cases we have studied, rotational energy either leaves the rate constant unchanged or causes it to decrease. More complete discussions of these reactions are beyond the scope of the present paper and will be given in future articles.

The significant rotational temperature dependences found for the reactant neutral have consequences for the interpretation of previous drift tube results. In the past, it has been common practice to measure rate constants for reactions of polyatomic ions as a function of kinetic energy in several buffers and to attribute the differences in rate con-
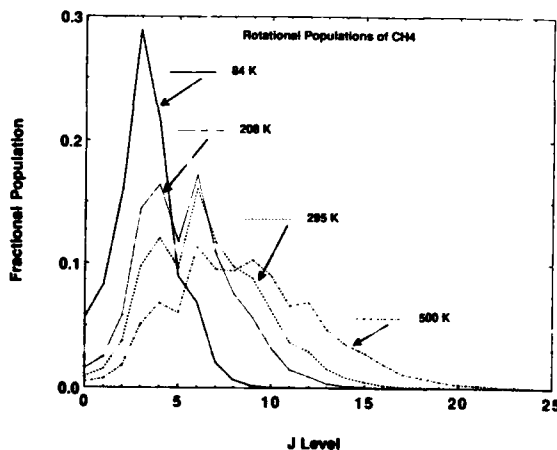

FIG. 3. Rate constants for the reaction of $O^- + CH_4$ vs the temperature of CH_4 at 0.06 and 0.25 eV.

FIG. 4. Rotational energy level populations of CH_4 at several temperatures.

stants to the differing degrees of ion vibrational excitation that could be expected to occur in the two buffers.[13] It was assumed that rotational energy of the reactant ion would have a negligible effect on the rate constants. Since rotational energy of the neutral sometimes appears to have a significant effect on rate constants, it is reasonable to expect rotational energy of the ions to be able to affect rate constants in the same manner. Substantial effects of rotational energy have recently been predicted theoretically for the reaction of $O_2^+ + CH_4$.[21] Effects of rotational energy have also been discussed for the reactions of N^+ and NH_3^+ with H_2.[22–24]

There are several examples of reactions in which the rate constant changes at a particular ion–neutral center of mass energy as the buffer is changed from He to Ar.[13] This has been interpreted as being due to the fact that there is more ion vibrational excitation in Ar than in He. Substantial differences in ion rotational temperatures are also expected in various buffers.[9,10] Energy dependences are usually plotted as rate constant vs center of mass kinetic energy of the reactants. This can be misleading since the internal energies of the ion are considerably different from the center of mass kinetic energy between the two reactants. The rotational energy is given by the center of mass kinetic energy between the ion and buffer.[9,10] The vibrational energy of the ion is less than or equal to this value.[9,11,12] The internal energies at a given center of mass kinetic energy with respect to the reactants are then substantially different in Ar and He buffers. Figure 5 shows the reactant ion rotational energy; i.e., the center of mass kinetic energy with respect to the buffer, vs reactant center of mass kinetic energy for O_2^+ reacting with CH_4 in Ar and He buffers. Large differences are seen. Both center of mass kinetic energies with respect to the buffer differ significantly from the reactant center of mass kinetic energy and from each other. The ratio between the buffer center of mass kinetic energies in Ar and He buffers, and therefore the ratio of internal energies of O_2^+ in these buffers, approaches a factor of 5 at high energy.

The change in rate constant in different buffers is attributed to the O_2^+ having more vibrational excitation in an Ar buffer than a He buffer. This has two causes. First, Ar is
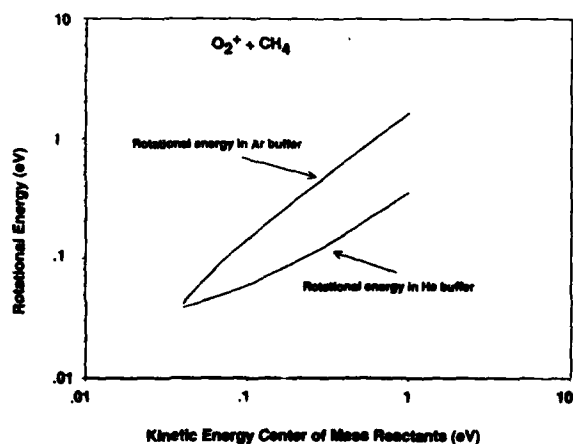

FIG. 5. Rotational energy of O_2^+ vs center of mass kinetic energy of the reactants for Ar and He buffers.

more efficient at exciting ion-vibrations than is He at a particular center of mass kinetic energy with respect to the ion–buffer collision. Secondly, at a particular reactant center of mass kinetic energy, the Ar–ion collision energy is greater than the He–ion collision energy, and vibrational excitation increases with increasing collision energy at the energies available in drift tubes. Ion rotations are also more excited in Ar than in He. In fact, as shown above, the rotational energy difference can approach a factor of 5 for the $O_2^+ + CH_4$ reaction. Assuming the same energy dependence ($E^{-0.5}$) as found in the $O^- + CH_4$ reaction, one would then expect the rate constant to decrease by a factor of 2.2 in changing from He to Ar buffer at high energies. What is observed instead is an increase of an order of magnitude. If the rotational dependence is appreciable this would mean that the difference due to vibrational excitation is even larger than previously thought. More complete discussions of the energy effects in this reaction are given by Durup-Ferguson et al.[14] and Troe.[21]

The results presented here do not negate the work that has been done on the influence of vibration on reaction rate. The effects due to rotation have so far been found to be small or in some cases negligible. The effects seen by changing the buffer are often dramatic.[13] The present work rather indicates that the situation is more complicated than previously thought. In fact, the vibrational contribution may be even larger than indicated previously since vibrational excitation usually seems to increase rate constants (but not always) and rotational excitation seems to have little effect or to decrease them. Therefore, the influence of vibrational excitation on a rate constant due to a change of buffer may be even larger than previously thought (for those reactions in which vibrational energy has been found to increase the rate constant) after rotational effects are factored out. Newer techniques alleviate this problem and directly measure dependences on the vibrational level at a particular energy and temperature.[14]

In conclusion, a technique has been described to derive the rotational temperature dependence of monatomic ion–polyatomic molecule reactions. This assumes that the vibrational modes of the reactant neutral are sufficiently high in energy that they are not appreciably excited at 500 K. We have found that in some cases rotational energy has a negligible effect on the rate constant and in others it decreases the rate constant by a factor of about $T^{-0.5}$. These are the first measurements of the rotational energy dependence of an ion–molecule reaction. The results bear on the derivation of the effects of vibration on ion–molecule reactions by studying a reaction in different buffers.

Note added in proof: The dependence of ion–molecule rate constants on rotational level has been discussed theoretically by T. F. Magnera and P. Kebarle, in Ionic Processes in the Gas Phase, edited by M. A. Almoster Ferreira (Reidel, Boston, 1984), p. 135. Their results are in agreement with the present experimental results.

ACKNOWLEDGMENTS

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