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:UMENTATION PAGE

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OMB No. 0704-0188

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE February 11,1992	3. REPORT TYPE AND DATES COVERED Reprint

4. TITLE AND SUBTITLE

The Effect of Low Frequency Vibrations in CH4 (Methane) on the Rate Constant for the Reaction of O_2^+ (X^2II_g, v=0) With CH4

Diatomic Oxygen(+) (X Square) S II sub g, V=0)) With Methane

5. FUNDING NUMBERS

PE 61102F
PR 2310
TA G2
WU 30

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8. PERFORMING ORGANIZATION REPORT NUMBER

PL-TR-92-2033

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FEB 28 1992
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES *Air Force Geophysics Scholar
Reprinted from J. Chem. Phys. 96(1), 1 January 1992

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; Distribution unlimited

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS Temperature dependence, Enhanced reactivity, Effective temperature	15. NUMBER OF PAGES 10
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	SAR

PL-TR-92-2033

The effect of low frequency vibrations in CH_4 on the rate constant for the reaction of O_2^+ ($X\,^2\Pi_g$, $v=0$) with CH_4

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(Received 2 August 1991; accepted 19 September 1991)

The rate constant for the reaction of O_2^+ with CH_4 has been measured as a function of average center-of-mass kinetic energy, $\langle KE_{cm} \rangle$, at several temperatures over the range 93–545 K. The rate constant decreases with increasing $\langle KE_{cm} \rangle$ at low $\langle KE_{cm} \rangle$ and increases at higher $\langle KE_{cm} \rangle$; the position of the resulting minimum depends on temperature. We have observed small differences in the rate constants measured at the same total $\langle KE_{cm} \rangle$ but at different temperatures in the low temperature regime ($T<300$ K). These differences, i.e., decreasing rate constants with increasing temperature, are discussed in terms of the possibility of a rate constant which is dependent upon rotational energy. At higher temperatures, 430 and 545 K, we find that the rate constant is significantly larger than that measured at lower temperatures at a given $\langle KE_{cm} \rangle$. This enhanced reactivity is attributed to vibrational excitation in the CH_4. From these data, we derive a rate constant for vibrationally excited CH_4 (in the low frequency modes) that is approximately a factor of 20 greater than the rate constant for the ground vibrational state. The data disagree with an early study of this type at low temperature. The disagreement is discussed, and arguments are presented which indicate that the earlier data are in error at low temperature with an applied drift field. The use of these data for deriving effective reaction temperatures in other nonthermal experiments is also discussed.

I. INTRODUCTION

The reaction of O_2^+ with CH_4 may be the most studied gas phase ion–molecule reaction involving more than three atoms. Numerous studies involving many different aspects of the reaction have been performed. The first measurement of the rate constants for this reaction was made in 1965 by Franklin and Munson.[1] Since that time the rate constant has been studied for its dependence on many parameters. Temperature dependences have been measured from 20 to 560 K,[2-4] energy dependences of the rate constant and cross section have been studied in beams[5] and drift tubes.[6-9] Dependences on the electronic[5,7,10] and vibrational states[8,10,11] of O_2^+ have been measured. Pressure dependences of the rate constant and branching ratio have been measured at low temperature.[4] Numerous studies have been carried out to elucidate the nature of the $CH_3O_2^+$ product ion.[12-17] The reaction has been studied using all of the partially and fully deuterated methanes.[18] Theoretical studies have been conducted.[18,19] This wealth of information has led to a fairly detailed understanding of the reaction mechanism.

Because of the abundance of information on this reaction one might think that little more could be added to the saga. Nevertheless, we have reexamined the reaction with the hope of adding insight into several of its aspects. We have recently developed a technique for deriving information on internal energy/temperature dependences of ion–molecule reaction rate constants or branching ratios.[20-23] The technique involves measuring the rate constant and/or branching ratio as a function of average ion–neutral center-of-mass kinetic energy ($\langle KE_{cm} \rangle$) in a selected ion flow drift tube. These drift tube measurements are made at several different buffer gas temperatures. Comparison of the rate constant or branching ratios measured at a particular $\langle KE_{cm} \rangle$ but different buffer gas temperature leads to a determination of the internal energy/temperature dependence of the measured parameter.

One of the first investigations in a variable temperature drift tube was a study of the rate constant for the reaction of O_2^+ with CH_4 (and CD_4) at the University of Birmingham.[24] The Birmingham workers found that their data could be fitted by the empirical expression $\Delta\langle KE_{cm} \rangle = 8k\Delta T_{eff}$, where the Δ indicates the kinetic energy added by the drift tube and the consequent added effective temperature. These results were interpreted in terms of energy randomization inside the reaction complex and the number of internal modes available. We have since realized that plotting data such as these versus center-of-mass kinetic energy can reveal information on internal energy effects.[20-23,25-27] When reanalyzing all available data for internal energy effects, we could not derive reasonable and consistent internal energy dependences from the Birmingham data. More consistent and reasonable dependences could be derived if we assumed that the Birmingham rate constants at 80 K with added drift field were too high by a factor of approximately 1.8, and either the 200 K drift data or the 420 K zero field rate constant were in error by smaller amounts.

With this in mind, and noting that the Birmingham data have recently been used in deriving effective temperatures in ion traps,[28] we decided to reexamine the reaction of O_2^+

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J. Chem. Phys. 96 (1), 1 January 1992 0021-9606/92/010275-10$06.00

with CH_4 using the Phillips Laboratory variable temperature-selected ion flow drift tube. This paper will focus on the possible effect of rotational energy in the methane molecule on the rate constant at low temperature and the effect of low frequency methane vibrations on the rate constant at temperatures where these vibrations are excited.

II. EXPERIMENT

The measurements were made using the Phillips Laboratory (formerly the Geophysics Laboratory) variable temperature-selected ion flow drift tube apparatus.[20] Instruments of this type have been the subject of review,[29] and only those aspects important to the present study will be discussed in detail. O_2^+ ions were created by electron impact on O_2 in a moderate pressure ion source (~0.1 Torr). The ions were extracted from the source and mass selected in a quadrupole mass filter. O_2^+ ions were injected into a flow tube one meter in length through an orifice of 2 mm diam. Helium buffer gas transported the ions along the length of the flow tube. The pressure in the flow tube was ~0.5 Torr. The buffer gas was added through a Venturi inlet surrounding the ion injection orifice. This type of inlet aids in injecting the ions at low energy. A drift tube, consisting of 60 electrically insulated rings connected by resistors, is positioned inside the flow tube. A voltage could be applied across the resistance chain in order to produce a uniform electric field along the axis of the flow tube for drift studies of $\langle \mathrm{KE_{cm}} \rangle$ dependences. The bulk of the gas in the flow tube was pumped by a Roots-type blower. The flow tube was terminated by a truncated nose cone. A small fraction of the ions in the flow tube was sampled through a 0.2 mm hole in the nose cone, mass analyzed in a second quadrupole mass spectrometer, and detected by a channel electron multiplier.

Neutral reactant gas was added through one of two inlets. The inlets are rings with a series of holes pointing upstream.[20] The area inside the ring is equal to the area outside the ring (between the ring and the flow tube wall) to aid in quickly distributing the reactant gas throughout the cross sectional area of the flow tube. Rate constants were determined from the decay of the primary ion signal as a function of added neutral flow. By combining the slope of the line obtained from a plot of the logarithm of the reactant ion signal versus neutral reactant flow, with the values of pressure, temperature, flow rates of the reactant and buffer, and ion velocity, a rate constant was calculated. A rate constant was determined at each of the two neutral inlets, and an end correction was determined from those data. The reported rate constant incorporates the end correction. Ion flight times were measured by applying an electrical retarding pulse to two of the drift tube rings separated by a known distance and measuring the difference in the two arrival time spectra of the ions. The ion velocity and therefore the reaction time were determined from these data and from knowledge of the relevant distances. Pressure was monitored by a capacitance manometer. Flow rates of the buffer and of the reactant gas were controlled and measured by MKS flow controllers. The entire flow tube could be heated or cooled over the range 85–570 K. All parameters, including ion velocity and the end correction, were measured for each rate constant determination.

The average kinetic energy in the ion-neutral center-of-mass system, $\langle \mathrm{KE_{cm}} \rangle$, in the drift tube is derived from the Wannier formula[30] as

$$\langle \mathrm{KE_{cm}} \rangle = \frac{(m_i + m_b)m_n}{2(m_i + m_n)} v_d^2 + \frac{3}{2} kT, \tag{1}$$

where m_i, m_b, and m_n are the masses of the reactant ion, buffer gas, and reactant neutral, respectively; v_d is the ion drift velocity; and T is the temperature. The first term in the formula is the energy supplied by the drift field, and the second term is the thermal energy. This formula is an excellent approximation of the ion energy at low ion energies.[26,31] At energies approaching 1 eV the formula is still good to within ± 10%.[26,31] The neutral reactant temperature under the conditions of the present experiments is the same as that of the buffer gas.

Two aspects of the experimental determination of the rate constants in this study warrant further discussion: the possible presence of vibrationally excited O_2^+ ions in the reaction region and the perturbation of the ion mobility by the added neutral reagent. These experimental complications may be related to the discrepancy found in the previous variable temperature drift tube measurements.

Some of the O_2^+ ions injected into the flow tube were internally excited. Early evidence for this excitation was the curvature observed in plots of the logarithm of the O_2^+ ion signal as a function of CH_4 flow.[8] Most of the excitation is vibrational[32] although a small amount of electronically excited O_2^+ may also have been present. For the purposes of this work, electronic and vibrational excitation behave similarly and are treated as vibrational excitation only. We were interested here in reactions of the ground vibrational and electronic state of O_2^+, and we therefore had to be careful to ensure that our rate constant determinations pertained to the ground state. About 20% of the injected O_2^+ ions were found to be in excited states.[32]

Three different procedures were used to measure the ground state rate constant. In the first procedure, rate constants were measured only under conditions of large O_2^+ depletion. CH_4 is known both to react more rapidly with O_2^+ ($^2\Pi_g$, $v>0$) than with O_2^+ ($^2\Pi_g$, $v=0$) and also to quench O_2^+ ($^2\Pi_g$, $v>0$).[8] Studying the reaction at larger depletions should therefore involve only O_2^+ ($^2\Pi_g$, $v=0$). The second and third procedures involved adding a quenching gas upstream of the reaction region in order to ensure that no vibrationally excited O_2^+ remained at the point of CH_4 addition. Two quenchants were used, CO_2 and O_2. The quenching rates for these gases are known,[33] and enough quenchant was added so that the percentage of O_2^+ ions in excited states was less than 1% at the start of the reaction zone. All three methods yielded rate constants that agreed with one another to within 10%, indicating that any remaining excited state O_2^+ did not affect the rate constants reported here within our experimental precision of ± 10%. The accuracy of the measurements is estimated to be ± 25%.

The second experimental problem arises when a drift field is applied. When the drift field is applied, the reaction time is very short (~0.5 ms) as compared with that with no drift field applied (~ 10 ms). This short reaction time coupled with the small reaction rate constant result in the need to add large flows of the neutral reagent, CH_4, to produce a large enough decline in the O_2^+ ion signal to measure an accurate rate constant. However, in a drift tube experiment it is desirable for the reactant gas concentration to be a small fraction of that of the buffer gas so that the ion transport properties (in particular, the mobility and the ion velocity distribution) are controlled solely by the buffer. Experience has shown us that, if the reactant gas concentration is less than approximately 1% of that of the buffer gas, this condition is generally met. In the experiments reported here, addition of 1% CH_4 to the flow tube caused curvature in the decay plots under some of the experimental conditions. The curvature observed was not of the type usually observed in this kind of experiment, i.e., upward curvature due, for example, to two states of differing reactivity, but was rather downward curvature where the reactant ion decay was steeper at large flows than at small flows. In this case, the curvature implied that the apparent rate constant increased at large CH_4 flows. Such curvature can arise from O_2^+ ($^2\Pi_g$, $v = 0$) ions having a smaller mobility in CH_4 than in He and therefore having a longer reaction time at larger neutral flows. Evidence supporting this explanation was revealed by measuring the ion flight times at different CH_4 flows. At small flows, the flight times were equal to those found for pure helium. At large flows, the flight times were longer. Because of this problem, the rate constants were sometimes measured with small depletion (a factor of 2) of O_2^+ ($^2\Pi_g$, $v = 0$) when quenchant was added. Tests to determine the regimes of CH_4 flow which did and did not affect the rate constants were performed by varying the maximum CH_4 flow used in determining a rate constant. For similar reasons, the amount of quenchant gas also was kept small enough so as not to affect the rate constant determinations. When only small depletions were required, the rate constant was determined many times in order to keep the error limits as small as possible.

Several other checks for consistency were performed. The flow velocity of the helium was varied both by changing the helium flow rate and by throttling a valve in the line to the Roots pump. Two grades of CH_4 were used, one of which was research purity (> 99.999% purity). Some "zero drift field" rate constants were measured with no added field and with a small added field such that $\langle KE_{cm} \rangle$ was negligibly affected. No effect was seen on the rate constants under any of these alternative conditions. Measurements at room temperature and above were repeated over a year apart and the agreement was within the stated 10% precision. The averages of the two sets of data are reported. Due to the presence of the excited states, no effort was made to study in detail the product ions, other than to determine that the main product ion is $CH_3O_2^+$, in agreement with many previous measurements.

III. RESULTS AND COMPARISON WITH PREVIOUS DATA

The present measured rate constants for the reaction of O_2^+ ($^2\Pi_g$, $v = 0$) with CH_4 are shown in Fig. 1 as a function of $\langle KE_{cm} \rangle$, as derived from Eq. (1). Circles, squares, circled pluses, triangles, and diamonds represent data obtained at 93, 170, 298, 430, and 545 K, respectively. Data obtained at a given temperature are connected by dashed lines. The pure temperature dependence (no drift field; $\langle KE_{cm} \rangle = 3/2kT$) is given by the solid line. Data obtained at the NOAA laboratory[6] at 300 K are shown for comparison and represented as pluses. There is excellent agreement between the present 298 K data and the NOAA data, the largest difference being on the order of 10%. We were not able to extend our measurements to very high drift fields due to the problems discussed in the experimental section. There is good agreement between the present data and the NOAA data at low $\langle KE_{cm} \rangle$. Good agreement with NOAA data has also been obtained in past work.[22,34,35] We are therefore encouraged to use the NOAA data at energies up to 0.1 eV for comparison to our higher temperature data.

As shown in Fig. 1, at the temperatures 93, 170, and 298 K, the rate constants obtained at similar center-of-mass kinetic energies are in reasonable agreement with each other, although some of the differences observed are just outside our estimated precision. At the temperatures above room temperature, i.e., 430 and 545 K, the rate constants at a given center-of-mass kinetic energy are significantly larger than the low temperature drift data. These effects will be discussed below.

Figure 2 compares the present data with the Birmingham data[2,24] mentioned in the introduction. Our data are shown by the same symbols as in Fig. 1. The Birmingham data at 80, 200, 420, and 560 K are shown as solid circles, solid squares, solid triangles, and a solid diamond, respectively. Note that rate constants at temperatures similar for the two data sets are represented by the same symbol distinguished by being open (present data) or solid (Birmingham). Both similarities and differences between the data sets from the two laboratories are apparent. The 200 K Birmingham data are in reasonable agreement with the present results at 170 and 298 K. The largest difference observed for these sets of temperature data, approximately 20%, is between the Birmingham zero field rate constant (the solid square farthest to the left in Fig. 2) and our value at approximately the same center-of-mass kinetic energy and at 170 K. Similarly the Birmingham rate constants at 420 and 560 K are smaller than the present results by about 20%. The largest difference between the data sets from the two laboratories, and the only difference which is outside the combined error limits, involves the Birmingham drift data at 80 K. In this case, the Birmingham rate constants at 80 K with added drift field are almost a factor of 2 larger than the present results obtained at 300 K (including the NOAA data) and below.

Which low temperature drift data set is correct? As stated in the introduction, the low temperature Birmingham data appeared to be in error when we analyzed the data for rotational and vibrational effects. If correct, the Bir-

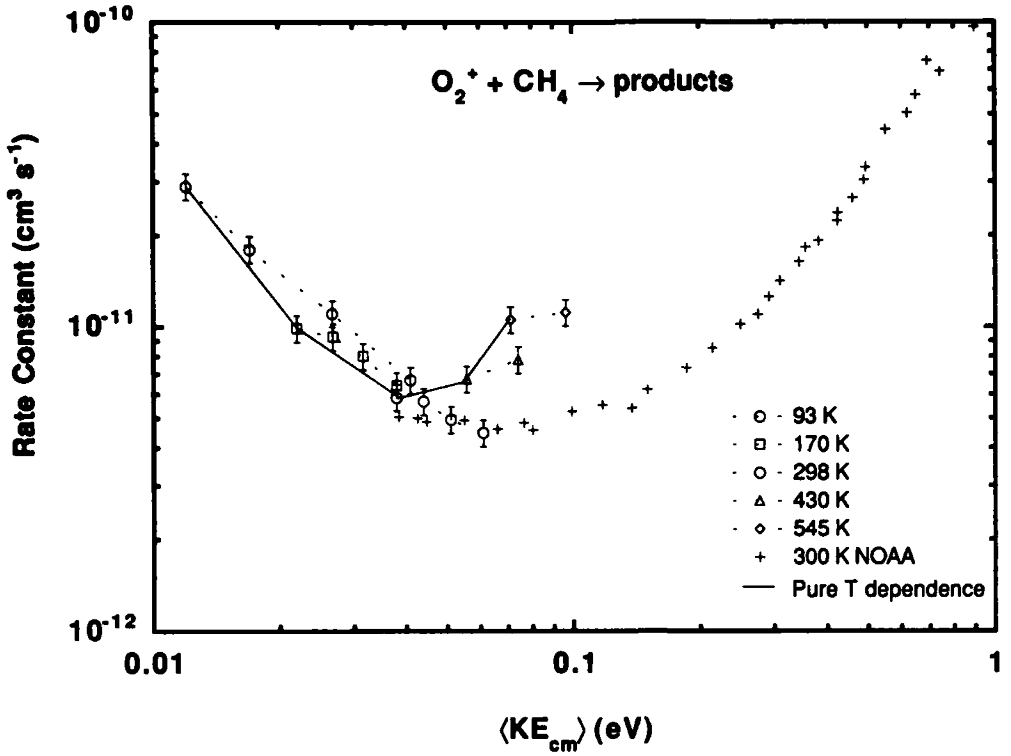

FIG. 1. Rate constants for O_2^+ ($^2\Pi_g$, $v = 0$) reacting with CH_4 as a function of ⟨KE_{cm}⟩. The present results are shown as open circles, open squares, circled pluses, open triangles, and open diamonds for data obtained at 93, 170, 298, 430, and 545 K, respectively. Data points obtained at a given temperature are connected by dashed lines. The pure temperature dependence (⟨KE_{cm}⟩ = $3/2kT$) is given by the solid line. Data obtained at the NOAA laboratory (Ref. 6) are shown as pluses. Error bars represent relative error only.

mingham data would imply a large negative rotational effect on the rate constant [rotations in either the O_2^+ ($^2\Pi_g$, $v = 0$) or the CH_4] between 80 and 200 K. This would be a much larger rotational effect than any that we have observed previously.[20-23,27,36] In contrast, the 420 K zero field point has approximately the same value as obtained at 200 K at similar center-of-mass kinetic energy, indicating a lack of rotational dependence between 200 and 420 K. This would imply that a large rotational dependence between 80 and 200 K almost vanishes between 200 and 420 K. However, some methane vibrations are excited at 420 K. Therefore, a positive vibrational effect could conceivably cancel a negative rotational effect. At a ⟨KE_{cm}⟩ of approximately 0.1 eV, the low temperature rate constant is largest, followed by the high temperature point, and that at 200 K is the lowest. If all of these rate constants were correct, unusual dependences on vibrational and rotational energy would be implied. In contrast, our data can be explained by simple vibrational and rotational effects as discussed in Sec. IV.

A comparison of all the available low energy data, as shown in Fig. 3, provides further evidence that the Birmingham low temperature data may be in error. In this graph, the present data at room temperature and below and the 300 K NOAA data are plotted together with the 80 K Birmingham data and with low temperature data obtained at the Max Planck Institute in Heidelberg[4] and at the CNRS in Meudon.[3] The latter two data sets refer to pure temperature dependences measured in apparatuses different from those used in the present measurements and in the Birmingham measurements. The rate constants from four of the 5 data sets and the 80 K zero field rate constant from Birmingham all fall approximately on a single smooth curve. However, the Birmingham rate constants at 80 K with added drift field do not fall on this curve and are significantly larger than the other measurements at similar center-of-mass kinetic energy. Based on the comparison between data sets taken at 4 other laboratories and the peculiar internal energy dependences implied by the Birmingham data, we suggest that, for the reaction of O_2^+ with CH_4, the rate constants taken in Birmingham at 80 K with the drift field on are incorrect.

The cause of the problem is less certain. Our apparatus and the Birmingham apparatus are very similar. As indicated in the experimental section of this paper, the rate constant for the reaction is very difficult to measure. Perhaps one of the experimental problems discussed above, such as the presence of vibrationally excited O_2^+ or the perturbation of ion mobility in the reaction region caused by the addition of large flows of CH_4, may have occurred during the Birmingham measurements. Another possibility involves evaluation of the end correction, necessary for the derivation of

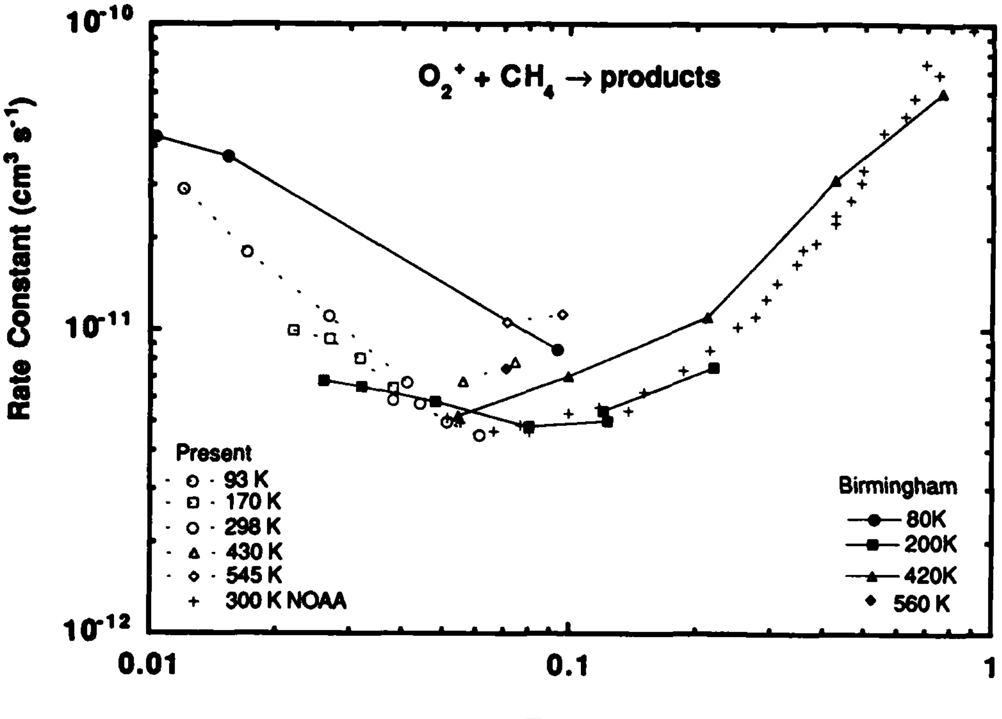

FIG. 2. Comparison of the rate constants for O_2^+ ($^2\Pi_g$, $v = 0$) reacting with CH_4 as a function of $\langle KE_{cm}\rangle$ for the present results and for those from the University of Birmingham (Refs. 2 and 24). The present results are shown as open circles, open squares, circled pluses, open triangles, and open diamonds for data obtained at 93, 170, 298, 430, and 545 K, respectively. Data obtained at a given temperature are connected by dashed lines. The Birmingham data are shown as solid circles, solid squares, solid triangles, and a solid diamond for temperatures of 80, 200, 420, and 560 K, respectively. Birmingham data obtained at a given temperature are connected by solid lines. Pluses refer to rate constants measured at 300 K in the NOAA laboratory (Ref. 6). Note that temperatures similar for the different sets of data are represented by similar symbols, i.e., solid symbols as compared with open symbols and pluses as compared with circled pluses.

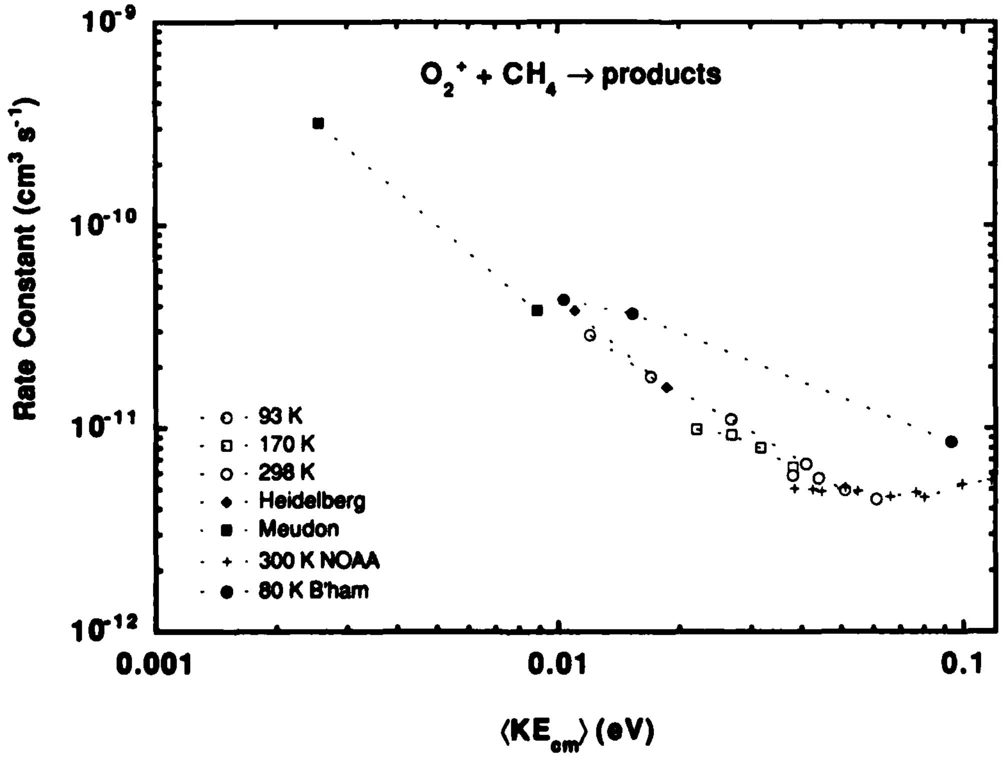

FIG. 3. Comparison of the rate constants for O_2^+ ($^2\Pi_g$, $v = 0$) reacting with CH_4 as a function of $\langle KE_{cm}\rangle$ measured at low temperature. The present results are shown as open circles, open squares, and circled pluses for data obtained at 93, 170, and 298 K, respectively. Pluses refer to rate constants measured at 300 K in the NOAA laboratory (Ref. 6). The Birmingham data (Ref. 24) at 80 K are shown as solid circles. Pure temperature data obtained at the Max Planck Institute in Heidelberg (Ref. 4) and the CNRS in Meudon (Ref. 3) are shown as solid diamonds and solid squares, respectively. Temperature is converted to $\langle KE_{cm}\rangle$ by $\langle KE_{cm}\rangle = 3/2kT$. Each data set is connected by dashed lines.

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the true rate constant. The Birmingham researchers report a small end correction at zero field, but they do not measure end corrections routinely at nonzero drift field.[37] We have found, however, that it is not always correct to apply the end correction determined at zero field to measurements made with the drift field turned on. Doing so can lead to errors in the rate constant, as discussed previously.[21,22]

The discrepancy between the Birmingham data and the present results is not severe. However, it does show that caution must be exercised in interpreting measurements conducted as a function of $\langle KE_{cm} \rangle$ in a drift tube at different temperatures. Unless one can measure accurately small differences between data points, it is easy to misinterpret differences between data obtained at different temperatures.

IV. VIBRATIONAL AND ROTATIONAL EFFECTS

It has recently been shown in our laboratory that dependences of rate constants or branching ratios on the internal temperature of the reactant neutrals can be derived for a variety of ion–molecule reactions from measurements of rate constants or branching ratios as a function of $\langle KE_{cm} \rangle$ at several temperatures.[20–23,25–27] For reactions of monatomic ions with neutrals, comparison of these rate constants or branching ratios at a particular $\langle KE_{cm} \rangle$ but at different temperatures gives information on the dependence of the measured reaction parameter on the internal energy/temperature of the reactant neutral. In the case of ions which are not monatomic, the interpretation is more complicated. Increasing the drift field not only increases $\langle KE_{cm} \rangle$ but also increases the internal energy of the reactant ion. In the present case of O_2^+ ($X\,^2\Pi_g$, $v = 0$) drifting at relatively low field strength, it is a good approximation that only the rotations of the O_2^+ are excited by either temperature or drift field.[38,39] The extent of excitation of internal degrees of freedom of the neutral gas, methane, is determined by the temperature of the buffer gas.

For buffer gas temperatures of 300 K and below, we observe small differences between rate constants measured at approximately the same center-of-mass kinetic energy but different temperatures, Fig. 1. Over the range studied, the 93 K rate constants are slightly larger than the rate constants obtained at 170 K, which are again slightly larger than are the rate constants at 300 K. The differences observed are just outside of our experimental precision. At these temperatures, there is very little vibrational excitation in the CH_4 molecules; at 300 K, only 0.7% of the CH_4 molecules are vibrationally excited.[39] An estimation of the effect of this level of excitation is given below.

Several possible explanations exist for the differences observed between the rate constants measured at a given $\langle KE_{cm} \rangle$ at temperatures of 93, 170, and 300 K. The simplest explanation is that either a random or systematic error could be the cause. We repeated the rate constant determinations under a variety of different experimental conditions (as described in the experimental section) and obtained the same results to within a few percent. Therefore, we believe it is unlikely that random error is the cause, but we cannot rule out a small (10–20 %) systematic error of unknown origin.

Alternatively, the differences might arise from slightly different ion kinetic energy distributions at different temperatures. Truly thermal ions will have Maxwellian distributions of energy. With an applied drift field the distributions are slightly different from Maxwellian, but it has been found both experimentally and theoretically that the distributions of ions in a drift tube incorporating a helium buffer are very nearly Maxwellian.[26,31,40–43] Nearly Maxwellian for the present purposes means that the rate constants measured in the drift tube are indistinguishable from those that would be found for a truly Maxwellian distribution. Since the rate constants are small and the differences at a particular $\langle KE_{cm} \rangle$ are also small, differing kinetic energy distributions at different temperatures cannot be ruled out as the cause of the differences.

The final possible explanation suggested is that the observed differences in the rate constants reflect the different rotational distributions in both O_2^+ ($^2\Pi_g$, $v = 0$) and CH_4 at a particular $\langle KE_{cm} \rangle$ at different temperatures. If this is the cause of the observed differences, then one can say that increasing rotational energy appears to decrease slightly the rate constant for this reaction.

Changes in the reaction rate constant for the reaction of O_2^+ ($^2\Pi_g$, $v = 0$) + CH_4 due to rotational energy effects is expected.[44] However, the magnitude and direction of these changes are uncertain, as discussed in detail by Troe.[44] This author investigated theoretically the rotational energy effects in this reaction and found two different effects on the reaction rate constant.[44] The reaction is expected to proceed through a double-well potential[18] with the central potential barrier a few hundred wave numbers below the energy of reactants.[44] Although the exact value of the barrier height is not known, it is expected that rotational energy in the reactants, as well as orbital angular momentum, will increase both this barrier height and the barrier height in the entrance (association) channel. Troe calculated the effect of rotational energy on the reactivity for several values of the barrier height. For most values of this height he found that rotational energy decreased the rate constant, although for some values of the barrier height, the presence of rotational energy led to a decrease of the rate constant at low rotational energy and an increase at higher rotational energy. Troe also calculated the effect of rotations on the number of open channels. Again he found that both positive and negative dependences can arise depending on the barrier height and total angular momentum. In light of the uncertainties in the details of the reaction surface, quantitative comparison of our results to the expected effects is not possible.

A possibility that can be tested is that rotational and translational energy have essentially the same effect on the reactivity. Figure 4 shows a plot of the present data and the NOAA data as a function of average total energy. For temperatures $\leqslant 300$ K this average total energy includes only rotational and translational energy (vibrational energy is negligible). Above 300 K, vibrational energy is added. The high temperature points are shown with and without the vibrational contribution. Rotational energy is given as $3/2\,kT$ for CH_4 and $2/3\langle KE_{cm} \rangle_b$ for O_2^+, where $\langle KE_{cm} \rangle_b$ is the barycentric energy of O_2^+ with respect to the buffer. Theory

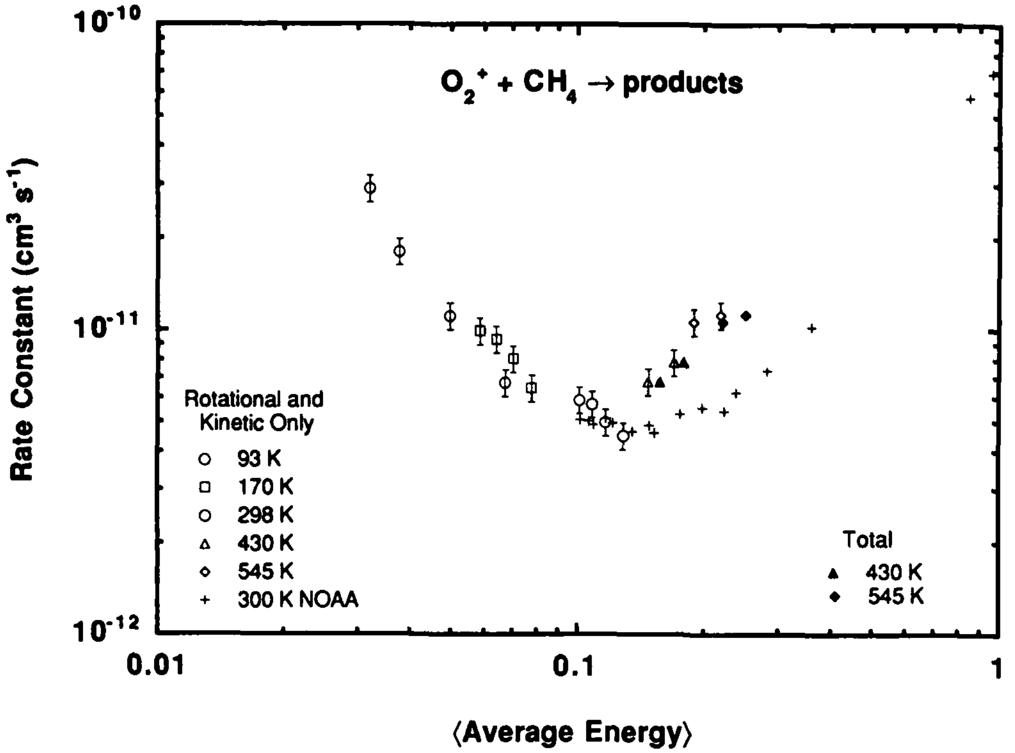

FIG. 4. Rate constants for O_2^+ ($^2\Pi_g$, $v = 0$) reacting with CH_4 as a function of average energy. Open points refer to average translational and rotational energy. Solid points refer to average translational, rotational, and vibrational energy. Circles, squares, circled pluses, triangles, and diamonds refer to data obtained at 93, 170, 298, 430, and 545 K, respectively. Data obtained at the NOAA laboratory (Ref. 6) are shown as pluses and refer to average translational and rotational energy. Error bars represent relative error only.

and experiment have shown that rotational temperature in a drift tube is given as $\langle KE_{cm} \rangle_b = 3/2kT$.[45] Vibrational energy is given as $\Sigma_n h\nu_n^* \,\mathrm{pop}(n)$, where pop($n$) is the population of the vibrational state, and ν_n are the vibrational frequencies. This expression ignores zero point energy, which only shifts the scale by a fixed amount. The symbols are the same as in Fig. 1. At low temperatures ($\leqslant$300 K) the data appear to fall approximately on one curve within experimental error, although there is not good overlap between the data sets. This suggests that rotational and translational energy behave similarly, although the data are not accurate enough to rule out small differences. We have observed similar behavior in the reactions of O^+ with CO_2,[36] and of Ar^+ with N_2.[23]

At temperatures above room temperature, large differences are observed between rate constants at similar center-of-mass kinetic energies or at similar total energies but at different temperatures. These differences are of the opposite sign to the trend observed at low temperature, i.e., the rate constant appears to increase with increasing temperature. Rate constants measured at a $\langle KE_{cm} \rangle$ of 0.71 eV at 545 and 298 K differ by a factor of about 2.3. Similar differences are found in the Birmingham data.[2,24] Differences of this magnitude due to varying kinetic energy distributions have never been observed in drift tube measurements in a helium buffer and have not been predicted theoretically.[26,31,40,46] Typically, differences due to varying kinetic energy distributions are expected to be on the order of less than 10%.[26,31,40–42,47,48] Although it appears that an explanation based upon varying kinetic energy distributions is highly unlikely, this explanation cannot be ruled out completely since the rate constants are small and the differences occur at the minimum in the rate constant curve. These conditions are expected to maximize a difference due to this cause.[26]

A more plausible explanation of our results is that the population of excited CH_4 vibrations at higher temperatures is responsible for the difference. At 430 K, 4.9% of the CH_4 molecules are vibrationally excited, and at 545 K, 12.4% are vibrationally excited.[39] These levels of excitation, together with reasonable rate constants for reaction of the vibrationally excited states, can explain the magnitude and direction of the differences in the observed rate constants. As stated in Sec. II, less than 1% of the O_2^+ ions are in excited states at the start of the reaction zone, even at the highest temperature and kinetic energy of these experiments. Vibrationally excited O_2^+, therefore, cannot account for the increased reactivity at higher energy.

An average rate constant for vibrationally excited CH_4 can be derived as follows. We assume that all of the difference between rate constants at a particular $\langle KE_{cm} \rangle$ but at different high temperatures is due to the differences in the population of excited levels of the CH_4 vibrations. Lumping the effect of vibrational excitation into a single parameter, the rate constant at a particular temperature is given as

$$k(T) = \mathrm{pop}_0(T)^*k_0 + \mathrm{pop}_1(T)^*k_1, \quad (2)$$

where $\mathrm{pop}_0(T)$ and $\mathrm{pop}_1(T)$ are the populations of the vibrational ground and excited states, respectively (1 refers to the fact that very little overtone excitation occurs), and k_0 and k_1 are the rate constants for the ground and vibrationally excited states, respectively. Since $\mathrm{pop}_0(T)$ and $\mathrm{pop}_1(T)$ can be calculated from the temperature and known frequencies of CH_4, and $k(T)$ is measured, k_0 and k_1 can be derived from data obtained at two temperatures. The only $\langle KE_{cm}\rangle$ for which data exists for three temperatures is 0.071 eV. Using the data at 430 and 545 K, one derives k_0 and k_1 as equal to 4.2×10^{-12} cm^3 s^{-1} and 7.3×10^{-11} cm^3 s^{-1}, respectively. One quantum of vibrational excitation in CH_4 increases the rate constant by a factor of ~ 17. A consistency check was performed by calculating the 300 K rate constant from Eq. (2) using the k_0 and k_1 derived above from the 430 and 545 K data and comparing it to the measured value. The resulting value of 4.7×10^{-12} cm^3 s^{-1} for the derived 300 K rate constant is in excellent agreement with the measured value. This analysis has been done at a particular $\langle KE_{cm}\rangle$ rather than a particular total energy. The difference between the two methods will be small since rotational effects have been shown to be small, particulary in the range where high temperature data exist. We estimate that the derived value of excited state rate constant is accurate to within a factor of 2.

The increase in the rate constant due to CH_4 vibrations is not the same in value as that observed for the addition of an equivalent amount of translational energy. For example, at $\langle KE_{cm}\rangle$ of 0.071 eV, adding the equivalent of one vibrational quantum of energy (0.16 eV) to $\langle KE_{cm}\rangle$ increases the rate constant for reaction with ground state methane by a factor of only ~ 2, to 1×10^{-11} cm^3 s^{-1} (see Fig. 1), as compared with a factor ~ 17 for reaction of vibrationally excited methane. Vibrational energy in the methane molecule is much more efficient in promoting reaction than translational energy. This is also seen clearly in Fig. 4 where adding the average vibrational energy to the translational and rotational energy shifts the points only slightly.

There are two modes that contribute to the vibrational excitation of CH_4 at the temperatures of these studies: a doubly degenerate ν_2 mode at 1534 cm^{-1} and a triply degenerate ν_4 mode at 1306 cm^{-1}.[39] The ν_4 mode contributes roughly 75% to the total vibrational excitation. Overtone excitations account for only a few percent of the total excitation. The observed effect may be due to some sort of weighted average of the ν_2 and ν_4 vibrations.

Over most of the energy range studied here the principal ionic product formed in the reaction of O_2^+ with CH_4 is CH_2OOH^+, although at the higher temperatures and energies, formation of CH_3^+ is also possible (via the high energy tail of the Boltzmann distribution of energies).[8,13] The rate limiting step in the mechanism to form CH_2OOH^+ ($+$H) and probably also CH_3^+ ($+HO_2$) is insertion of the O_2^+ into a C–H bond.[13] Any form of energy that significantly increases the C–H bond length is likely to enhance reactivity greatly. The normal vibrational modes of CH_4 are shown in the text by Herzberg.[49] The ν_4 mode is a combination stretch and bend. Stretching in this mode should facilitate the bond insertion step. The ν_2 mode is a bending mode, and the effect on the reactivity is harder to predict.

Earlier in this section we discussed small differences between the rate constants measured at 93, 170, and 300 K with varying kinetic energy. The vibrational analysis indicates that the rate constants at 300 K are enhanced by vibration excitation. Therefore, comparison of our low temperature data to reveal rotational energy effects on the rate constant requires eliminating (subtracting) the $\sim 11\%$ vibrational enhancement of the rate constant observed at 300 K. Lowering the 300 K rate constants accordingly enlarges the differences observed at low temperature, further suggesting that the differences are systematic in nature and perhaps related to a rotational dependence. This, however, does not affect the total energy analysis.

While these are the first measurements of the effect of CH_4 vibrations on this reaction, several studies have considered the effect of O_2^+ vibrations on the reactivity. The first qualitative results were those of Alge *et al.*[9] who showed that vibrational excitation of O_2^+ enhances the reactivity. Durup-Ferguson *et al.*[8] have studied the competition between quenching and reactivity for vibrationally excited O_2^+. They found that O_2^+ ($v \geqslant 2$) reacts very rapidly and that O_2^+ ($v \geqslant 3$) reacts mainly by charge transfer. They also found that O_2^+ ($v = 1$) is rapidly quenched by CH_4. Tanaka *et al.*[11] studied the effect of O_2^+ vibrational excitation on the cross section of this reaction for O_2^+ ($v = 0$–3) at an energy of 0.27 eV. They found that the channel producing CH_2OOH^+ increases with O_2^+ vibrational level from $v = 0$ to $v = 2$ and decreases for $v = 3$. This decrease for $v = 3$ is more than compensated by large increases in the cross sections for the endothermic channels producing CH_3^+ and CH_4^+. They also found that vibrationally excited O_2^+ increases the overall reactivity by approximately the same amount as does translational energy. This is in contrast to our findings that CH_4 vibrations are more efficient than translational energy at promoting the reaction. At higher energy (4.9 eV), Lindsay *et al.*[10] found that the charge transfer cross section is fairly insensitive to the O_2^+ vibrational state.

V. IMPLICATIONS FOR EFFECTIVE TEMPERATURE MEASUREMENTS

It has been suggested that measurements such as those presented here can be used to estimate effective temperatures in ion traps.[50] Recently, the reaction of O_2^+ with CH_4 has been used to calculate the effective temperature in a quadrupole ion trap experiment.[28] The derivation was based on the equation $\Delta\langle KE_{cm}\rangle = 8k\Delta T$ derived from the Birmingham data[24] which, as we have shown, most probably contain errors. In fact, our data do not confirm this empirical formula at low temperature. We maintain that the concept of a single effective temperature for this reaction is incorrect and any value so derived will surely not provide an appropriate effective temperature for any other arbitrary reaction (except by coincidence).

The present data show that different kinds of energy can have differing effects on the reactivity. In nonthermal experiments such as drift tubes, ion traps, and beams, one must refer to different effective temperatures for each type of energy. The present experiments involve an effective kinetic temperature related to $\langle KE_{cm} \rangle$, true vibrational and rotational temperatures of CH_4 given by the gas temperature, an effective rotational temperature of O_2^+ given by $\langle KE_{cm} \rangle_b$, the average ion-buffer center-of-mass kinetic energy,[45] an effective vibrational temperature of O_2^+ controlled by the amount of quenchant added, and an electronic temperature partially determined by the ion source conditions and amount of added quenchant. Thus, five different effective temperatures (for 6 types of energy) are necessary to describe our drift tube experiments. Fortunately, these effective temperatures are known and very similar to real temperatures (in a helium buffer) in the drift tube. This is important in separating the effects of each kind of energy on the reactivity. In other experiments, different conditions will apply, and the concept of effective temperatures must be carefully defined.

In the ion trap experiments a rate constant of 8.2×10^{-12} $cm^3 s^{-1}$ and a branching ratio were measured for the reaction of O_2^+ with CH_4, and an effective temperature of 600–700 K was derived.[28] However, the ion trap measurements were made at 300 K and the extra energy added by the trap is kinetic energy. A more appropriate diagnosis would have been either to use the empirical expression derived by the Birmingham group to evaluate the added kinetic energy or to compare the results with the NOAA 300 K drift tube measurements[6] to evaluate the average center-of-mass kinetic energy. We estimate that the relative translational energy given to the ions in the ion trap experiments was ~0.2 eV based on the NOAA data.[6]

VI. CONCLUSIONS

We have measured the rate constant for the reaction of O_2^+ ($X\,^2\Pi_g$, $v = 0$) with methane over a wide range of temperature and drift energies. We believe that by comparing rate constants at a particular $\langle KE_{cm} \rangle$ but at different temperatures, one can quantitatively derive and assign internal energy effects (assuming that effects due to the ion velocity distribution are negligible) as we have demonstrated in the past.[20-23,25-27] Analyzing our data on this reaction, we find that the rate constant appears to be enhanced by vibrational excitation in methane and may be diminished by a smaller amount by rotational excitation.

We have provided evidence that rate constants derived previously from low temperature drift tube measurements for the reaction of O_2^+ with CH_4 (Ref. 24) are in error. The present low temperature data do not confirm the previously derived empirical expression $\Delta\langle KE_{cm} \rangle = 8k\Delta T_{eff}$. In addition, such an empirical expression does not provide a physical understanding of these varying rate constants. Finally, any such empirical correlation will depend both on the reaction and on the experimental conditions and cannot be arbitrarily applied to other reactions, although similar correlations (in form) may be expected for reactions with similar mechanisms.

It is probably safe to say that the rate constant for this reaction has been studied experimentally for dependences on more types of energy than that for any other ion–molecule reaction. The dependences are summarized below.

Translational energy of O_2^+ ($X\,^2\Pi_g$): Several experiments have shown that increasing the relative translational energy of the reaction partners decreases the rate constant at low temperatures and energies.[2,5,6,8,9,24] A broad minimum in the value of the rate constant is observed at about 0.04 eV. At energies above 0.1 eV the rate constant increases dramatically; the increase has been attributed to new product channels becoming accessible.[8]

Rotational energy: The present low temperature drift data suggest that addition of rotational energy results in a small decrease in the reaction rate constant, or efficiency. A plot of rate constant versus total energy suggests that rotational and translation energy have similar effects on reactivity. However, definitive assignment of the observed rate constant variations to rotational energy effects is not possible.

O_2^+ vibrations: Several studies have been made of the effect of O_2^+ vibrations.[8-11] At an energy of 0.27 eV, the reactivity to produce CH_2OOH^+ increases with O_2^+ vibrational level from $v = 0$ to $v = 2$. For O_2^+ ($v = 3$) a dramatic increase in the reactivity is found as compared with O_2^+ ($v = 0$), and the major product changes to CH_4^+.[8,11] At an energy of 4.9 eV the charge transfer cross section appears to be fairly insensitive to the reactant O_2^+ vibrational state.[10]

CH_4 vibrations: The present study indicates that vibrational excitation in the ν_4 and/or ν_2 modes of methane greatly increases the efficiency of the reaction with O_2^+ to form CH_2OOH^+. The rate constant appears to increase by a factor of almost 20 over that for the ground state when the reactant CH_4 has an average of one quantum of excitation in these vibrational modes.

O_2^+ electronic energy: The electronic state O_2^+ ($a\,^4\Pi_u$), which is 4 eV higher in energy than the ground state, has been found to react orders of magnitude faster than the ground state, O_2^+ ($X\,^2\Pi_g$).[5,7,10] The major product ions observed in the reaction of the excited state ion are CH_4^+ and CH_3^+, the same as are observed for reaction of the ground state ion at higher translational energies.[5] At high energies, 3–300 eV, the cross section for charge transfer for the $a\,^4\Pi_u$ state remains larger than that for the ground state, approximately three times the ground state value.[10]

Translational energy of electronically excited O_2^+: Translational energy has been found to have little effect on the reactivity of O_2^+ ($a\,^4\Pi_u$) towards methane.[7,10] The rate constant at room temperature is collisional, so that no enhancement is expected. The cross section for charge transfer of the $a\,^4\Pi_u$ state also appears to be relatively insensitive to the relative translational energy of the reactants.[10]

Pressure: Bohringer and Arnold[4] found that the rate constant increases with increasing pressure at low temperatures. These observations have been explained in terms of interaction of the third body with the reaction complex.[18] The reaction complex lives long enough in the first potential energy well that collisions with the buffer gas remove some energy, thus increasing the likelihood of reaction. Bohringer and Arnold also observed clustering.

Although some aspects of this reaction have been theoretically modeled previously,[18,44] the wealth of information on this reaction should make the idea of a detailed and comprehensive theoretical study both attractive and possible. We look forward to such a study.

ACKNOWLEDGMENTS

This research was sponsored in part by the Phillips Laboratory, United States Air Force, under Contract No. F19628-86-C-0224. The United States Government is authorized to reproduce and distribute reprints for governmental purposes notwithstanding any copyright notation herein.

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