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Citation: The Journal of Chemical Physics **81**, 2657 (1984); doi: 10.1063/1.447975
View online: http://dx.doi.org/10.1063/1.447975
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Competitive reaction and quenching of vibrationally excited O_2^+ ions with SO_2, CH_4, and H_2O

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(Received 7 March 1984; accepted 16 May 1984)

Vibrationally excited O_2^+ ions injected into a He buffered flow tube react rapidly with SO_2 and H_2O by charge transfer and with CH_4 to produce $CH_3O_2^+$, CH_3^+, and CH_4^+. It is found that the rapidly reacting states at thermal energy are $O_2^+(v>2)$ for SO_2 and CH_4 and $O_2^+(v>3)$ for H_2O, while the lower vibrationally excited states are rapidly quenched. When the reactions of SO_2 and CH_4 are studied in Ar buffer as a function of kinetic energy it is found that the vibrational temperature of O_2^+ established through collisional excitation by the Ar buffer is perturbed by quenching collisions with the reactant molecules. This leads to observed reaction rate constants that change with reactant gas concentration. For the reaction of O_2^+ with CH_4 the influence of kinetic and vibrational energy on the branching ratio of the reaction channels has been investigated. The present vibrational relaxation data for $O_2^+(v)$ by CH_4, in conjunction with other recent measurements, allows a rather detailed picture of the mechanism to be drawn for this complicated reaction that involves the making and breaking of four chemical bonds.

I. INTRODUCTION

A number of reactions of vibrationally excited ions have been carried out in ion swarm experiments at kinetic energies from thermal to ~ 1 eV.[1-4] Recently, studies of vibrational relaxation of diatomic ions have been carried out in similar experiments.[5-7] The present measurements represent an extension of these studies to the interaction of vibrationally excited O_2^+ ions with the molecules SO_2, CH_4, and H_2O, in which competition is found between reaction and vibrational quenching channels. This competition leads to a considerable increase in the complexity of the studies.

Viehland *et al.*[8] have shown that the internal degrees of freedom of molecular ions drifting in atomic buffer gases can be assigned an internal temperature T_i controlled by the relative ion–buffer gas kinetic energy in steady state. Studies on several triatomic ions showed that vibrational steady state was obtained in $\sim 10^3$ collisions with Ar buffer gas in a drift tube, but that the ions were not vibrationally excited in He buffer gas.[4] Direct measurement of O_2^+ vibrational relaxation rate constants in He and Ar buffer gases show that O_2^+ ions will attain a steady state vibrational population in Ar in experiments such as the present one involving more than 10^3 ion–buffer collisions and that O_2^+ ions will not be vibrationally excited in He buffer gas.[5,6] Earlier experiments showed a large enhancement in the rate of reaction of O_2^+ ions with CH_4 in Ar relative to He[1-3] due to vibrational excitation. At that time, vibrational quenching experiments with added O_2 showed directly that the O_2^+ ions were vibrationally excited in Ar and not in He.[2]

Introducing ground state O_2^+ ions into a He buffer in a flow drift tube allows rate constant measurements to be made for ground vibrational state O_2^+ ions as a function of kinetic energy. There is a large enhancement of the rate constant with kinetic energy for the exothermic reaction $O_2^+ + CH_4$[1-3] and, of course, for the endothermic charge transfer of O_2^+ with SO_2 and H_2O. On the other hand, when a distribution of vibrationally excited O_2^+ ions is injected into the flow tube, both the reaction and quenching rate constants can be determined separately for different vibrational states, using the monitor ion technique for the detection of ions in selected vibrational levels.[5]

In Ar buffer gas the situation is more complex. Any vibrationally excited O_2^+ ions injected into an Ar buffer will be rapidly quenched, due to the large quenching rate constant $1.0(-12)$ cm^3 s^{-1} for $O_2^+(v=1)$ and $2.5(-12)$ cm^3 s^{-1} for $O_2^+(v=2)$.[5,6] Above thermal energies, the O_2^+ ions will be collisionally excited in the Ar buffer and will attain a steady state vibrational population by excitation and deexcitation in collisions with Ar. The population will be Boltzmann with a temperature T_i given by $3/2\, k_B T_i = KE^B_{cm}$, where k_B is Boltzmann's constant and where KE^B_{cm} is the O_2^+–Ar center-of-mass kinetic energy, controlled by varying the drift tube electric field and buffer gas pressure. This would be an ideal situation for the quantitative determination of the vibrational enhancement of the rate constant except for the fact that this steady state is perturbed by the addition of the reactant gas, since CH_4 is a far more effective vibrational quencher than Ar. Thus, the O_2^+ vibrational temperature will depend on the CH_4/Ar ratio, i.e., the temperature will vary in the course of adding CH_4 to measure the $O_2^+ + CH_4$ rate constant. This complication was not appreciated in the earlier studies.

The present study was undertaken, in light of the recent gains in understanding, in order to see what mechanistic reaction details can be derived from competitive reaction and quenching studies. The emphasis is on the very complex O_2^+ reaction with CH_4. The present results, in combination with a great wealth of other recent data on this reaction, provide a quite detailed picture of a remarkably complex reaction.

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II. EXPERIMENTAL

The studies have been conducted in a flow-drift tube (FDT)[9] with a mass-selected ion source.[10,11] This apparatus has been used for the study of many ion–molecule reactions as a function of kinetic energy.[1,2,9] The basic experimental approach to studying vibrationally excited O_2^+ ions in the FDT is outlined in Ref. 5. A summary of this approach is included here along with specific features of the present measurements.

Unless stated otherwise, the O_2^+ primary ions in the present study have been produced in a remote electron–impact ion source. The energy of the ionizing electrons was maintained at 15.4 eV to avoid the production of metastable $O_2^+(a\,^4\Pi_u)$ ions.[5] After mass selection, the primary ions were injected into the flow tube with the aid of a venturi inlet.[10,11] For He and Ne buffer gases, vibrationally excited O_2^+ ions produced in the ion source were found not to be quenched in $\sim 10^4$ collisions in the FDT.[5] The vibrational state distribution of the O_2^+ ions in the FDT was probed by means of charge-transfer reactions with Xe, SO_2, and H_2O. The charge-transfer reactions are exothermic for $O_2^+(v\geqslant 1)$, $O_2^+(v\geqslant 2)$, and $O_2^+(v\geqslant 3)$ ions, respectively. With slight variation ($\pm 3\%$), the following state distribution was found: $O_2^+(v=0)\approx 35\%$, $O_2^+(v=1)\approx 43\%$, $O_2^+(v=2)\approx 11\%$, and $O_2^+(v\geqslant 3)\approx 11\%$.

For the measurements of the ground state reaction rate constants of $O_2^+(v=0)$ with SO_2 and CH_4 as a function of kinetic energy in He, the primary ions were produced by 100 eV electrons. The excited O_2^+ ions were removed by adding traces of CO_2 or O_2 to the buffer gas. The electronically excited metastable ions of O_2 react rapidly with CO_2 [$k = 9(-10)\,\mathrm{cm^3\,s^{-1}}$][12,13] and are rapidly deexcited in collisions with O_2 [$k = 3.1(-10)\,\mathrm{cm^3\,s^{-1}}$].[12,13] The vibrationally excited ions are rapidly quenched by CO_2 and O_2 with rate constants of $1(-10)$ and $3(-10)\,\mathrm{cm^3\,s^{-1}}$, respectively.[5,6]

The ions injected into the FDT were carried downstream by the fast flowing buffer gas through a field free region and into a drift region with a length of 55.9 cm. Reactant and quenching gases are added in the latter at a gas inlet port located 48.4 cm upstream of the detection system. The monitor gases for probing the vibrational state distribution of O_2^+ were added at a port 3 cm upstream of the detection system. The flow tube pressure was maintained at 0.25 and 0.4 Torr with a He buffer, at 0.2 Torr with a Ne buffer, and at 0.125 and 0.2 Torr with an Ar buffer. The measurements were carried out at gas temperatures of 297 to 300 K.

In contrast to the experiments in He and Ne buffer gases, vibrationally excited O_2^+ ions are completely quenched to the ground state in an Ar buffer in the flow tube region preceding the drift-reaction region. This follows from the measured quenching rate constant[5,6] for Ar of $k_q = 1(-12)$ $\mathrm{cm^3\,s^{-1}}$, the residence time of the O_2^+ ions $\tau \geqslant 4(-3)$ s, and an Ar density of about $6(15)\,\mathrm{cm^{-3}}$. $O_2^+(a^4\Pi_u)$ ions are destroyed even more rapidly[12,13] by charge transfer with the Ar buffer [$k = 5(-10)\,\mathrm{cm^3\,s^{-1}}$]. At sufficiently high kinetic energy, O_2^+ ions are vibrationally excited in an Ar buffer with a vibrational state distribution described by temperature T_i.[8] This temperature is equivalent to the mean, center-of-mass kinetic energy in the collisions of the ions with the buffer gas atoms KE_{cm}^{B}:

$$\tfrac{3}{2}k_B T_i = KE_{\mathrm{cm}}^{B} = \tfrac{3}{2}k_B T + \tfrac{1}{2}M_B v_d^2, \tag{1}$$

where T is the gas temperature, M_B is the mass of the buffer atoms, and v_d is the measured drift velocity of the ion. The theory applies when there are enough collisions of O_2^+ with the buffer to reach a steady state between excitation and quenching.

The rate constant k_{q1} of the quenching process with quench gas Q:

$$O_2^+(v=1) + Q \rightarrow O_2^+(v=0) + Q \tag{2}$$

was measured by the monitor ion technique that has been described earlier.[5] In these measurements, a fixed flow of Xe is added at the monitor gas inlet to convert some of the vibrationally excited $O_2^+(v\geqslant 1)$ ions to Xe^+ "monitor ions." The Xe^+ ion signal at the detector is then proportional to the concentration of vibrationally excited O_2^+ ions at the end of the FDT (except for a small contribution to the Xe^+ signal from the slowly reacting ground state O_2^+ ions, which is corrected for). If a quench gas is added to the FDT upstream of the monitor gas inlet, the monitor signal recorded as a function of quenching gas flow shows a decline that reflects the quenching rate constant k_{q1} (when the presence of vibrational states $v\geqslant 2$ is neglected, which can be done without introducing a large error[5]).

In the present case of quenching by SO_2, CH_4, and H_2O, the situation is more complex because these gases also react with the upper vibrational levels of O_2^+. For this case, the monitor ion signal recorded as a function of quenching/reactant gas addition shows a decline which reflects both the reaction rate constants of the upper vibrational levels and the quenching rate constant k_{q1} (quenching of $v=2$ and $v=1$ in the case of H_2O). Thus, for the data analysis in the present study, the monitor ion technique used previously was modified. The quenching rate constant can be deduced more directly from the O_2^+ signal as a function of quenching/reactant gas flow when sufficient monitor gas is added. For this case, the difference between the O_2^+ signal as a function of quenching/reactant gas flow and the O_2^+ signal at large flow shows a decline that closely reflects the quenching rate constant k_{q1}. With a small correction, the quenching rate constant can be deduced exactly. This procedure is explained mathematically in the Appendix.

To treat the more complex case of $O_2^+ + CH_4$, where there is also a nonnegligible ground state reaction, a numerical model that simulates all the reaction and quenching processes involved has been used to find the quenching rate constants by fitting the calculated results to the measured data. The model includes three different states of O_2^+ with a distribution $(v=0)=33\%$, $(v=1)=45\%$, and $(v>2)=22\%$. The states of $v=2$ and $v>2$ were not distinguished since they have essentially the same reaction rate coefficients with CH_4. Results of the model calculations are shown along with the corresponding experimental data in Fig. 1. Further input data for the model calculation are the fractions of ground state and excited state O_2^+ ions that are converted to the monitor ion Xe^+ before detection for the fixed flow of Xe gas

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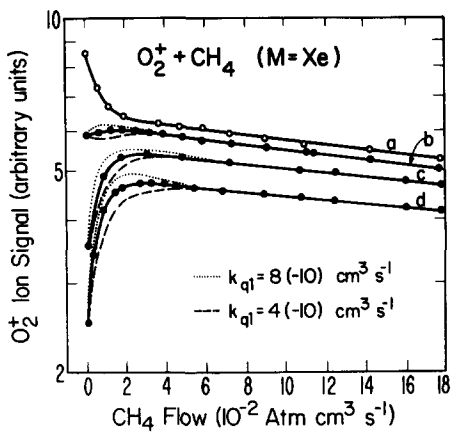

FIG. 1. Variation of the primary ion O_2^+ signal as a function of quenching/reactant gas CH_4 addition (points and solid curves). For (a) no monitor gas is added while (b), (c), and (d) were obtained with different constant flows of Xe monitor gas. Model calculations simulating the situation have been fitted to these data with the parameters $k_g = 6(-12)$ cm^3 s^{-1}, $k^* = 7(-10)$ cm^3 s^{-1}, and a vibrational state distribution of $(v=0) = 33\%$, $(v=1) = 45\%$, and $(v=2) = 22\%$. The values $k_{q1} = 4(-10)$, $6(-10)$, $8(-10)$ cm^3 s^{-1} have been used in the calculations. The curves for $k_{q1} = 6(-10)$ cm^6 s^{-1} are almost identical to the experimental data and thus are not shown.

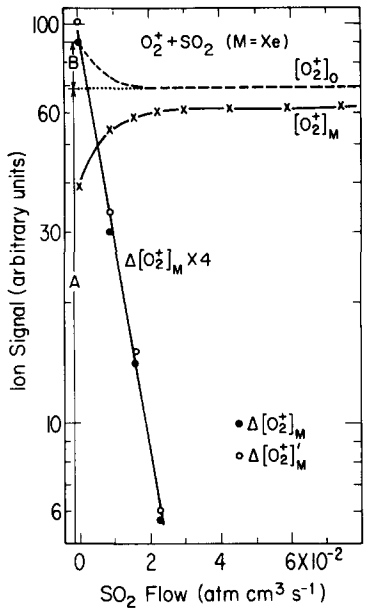

FIG. 2. Variation of the primary O_2^+ ion signal as a function of quenching/reactant gas SO_2 addition. Curve $O_2^+(M)$ is with and curve $O_2^+(0)$ without the addition of a constant flow of Xe monitor gas. Full circles show the parameter $\Delta O_2^+(M)$ which is the difference between $O_2^+(M)$ and $O_2^+(M)$ when $[SO_2] = \infty$. Open circles are the corrected values $\Delta O_2^+(M)'$ (see the Appendix). The quenching rate constant $k_{q1}(SO_2)$ is deduced from the linear decline of $\Delta O_2^+(M)'$.

in the measurement (these fractions are denoted R' and R in the Appendix). These two factors are determined empirically as described in Ref. 5 for each case (b), (c), and (d) shown in Fig. 1. The model calculations also give a good measure of the sensitivity of the modified monitor ion technique. The model calculations have therefore also been applied to test the SO_2 and H_2O quenching results.

III. RESULTS AND DISCUSSION

A. $O_2^+ + SO_2$

SO_2 reacts with O_2^+ by charge transfer, which is exothermic by 0.19 eV for O_2^+ $(v=2)$ and slightly endothermic by 0.039 eV for O_2^+ $(v=1)$. As has been shown,[5] a fast and a slow reacting group of O_2^+ ions can be distinguished experimentally in a He buffer at near thermal energy. The proportion of the two groups of ions is obtained by recording the primary ion signal as a function of reactant gas addition and extrapolating the final slope of the O_2^+ signal for large flows back to zero flow in a semilogarithmic plot as indicated in Fig. 2. The fraction of fast reacting ions is designated by B and the slow reacting fraction by A in Fig. 2. The fractional abundance of the fast reacting ions in the $O_2^+ + SO_2$ reaction is found to be $B/(A+B) = 22\%$ at thermal energy. If the kinetic energy of $O_2^+ - SO_2$ collisions is increased, the fraction of fast reacting O_2^+ ions in a He buffer increases to 40% at 0.4 eV as shown in Fig. 3.

The rate constant that is deduced from the final slope of the O_2^+ ion signal as a function of reactant gas flow (Fig. 2) will be designated by k_g, the reaction of the ground state O_2^+ ions. The curve that is obtained by subtracting the straight line fitted to the final slope from the primary ion signal curve gives another rate constant that will be designed by k^* (see Fig. 4 for the example of the $O_2^+ + CH_4$ reaction and Ref. 5). k^* corresponds to the rate of disappearance of the fast reacting ion species.

At thermal energy, a rate constant k^* of $1.2(-9)$ cm^3 s^{-1} is determined.[5] k^* is the sum of the reaction rate constant k_2 and the quenching rate constant k_{q2} for the O_2^+ $(v \geqslant 2)$ ions.[5,13] Unfortunately, the two rate constants cannot be determined independently. If one assumes that the vibrational distribution of the O_2^+ ions given by the Franck–Condon factors[14] is an upper limit to the vibrational excitation in the present experiment, one obtains O_2^+ $(v \geqslant 2) \leqslant 45\%$ and $k_2 \geqslant k_{q2}$. k^* was found to be constant in the energy range from thermal energy to 0.2 eV.

The reaction rate constant of the charge transfer of O_2^+ $(v=0)$ with SO_2 as a function of kinetic energy has been measured and the results are shown in Fig. 5. The rate constant is steeply increasing with energy as expected for an endothermic reaction. At energies below 0.1 eV, O_2^+ associates with SO_2 and therefore no values for the charge transfer reaction rate constant are given for this energy range.

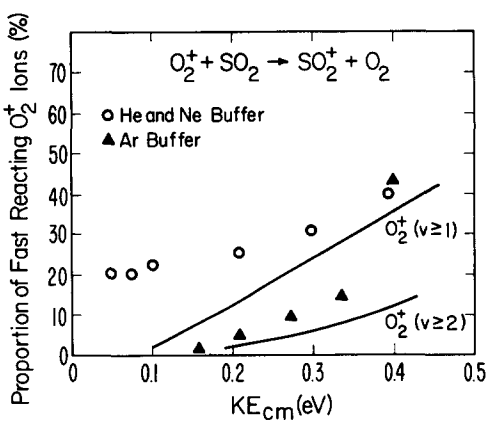

FIG. 3. Fraction of $O_2^+(v)$ ions reacting fast with SO_2 as a function of relative kinetic energy with respect to ion-reactant collisions KE_{cm}^R, in He, Ne, and Ar buffers. In He and Ne buffers the O_2^+ ions have the vibrational state distribution they attained prior to injection (see the text) while in the Ar buffer the excitation is determined by collisions with the buffer. The vibrational state distribution calculated for the O_2^+ ions in the Ar buffer at excitation and deexcitation steady state (solid lines) is shown for comparison.

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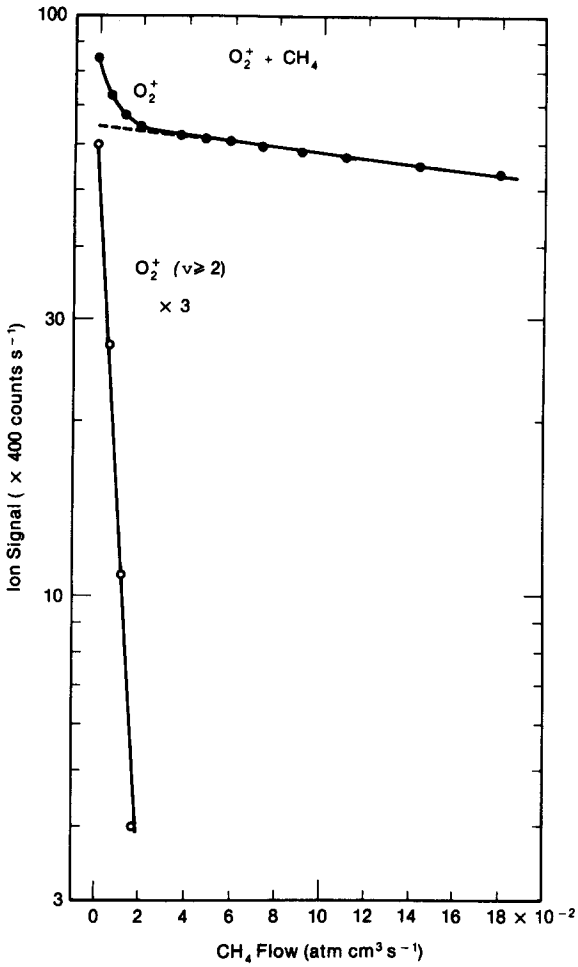

FIG. 4. Reaction of CH_4 with O_2^+ ions in the given vibrational state distribution in the He buffer at near thermal energy. The dashed line gives the ground state rate constant k_g, while the steep straight line gives k^* for O_2^+ ($v \geq 2$).

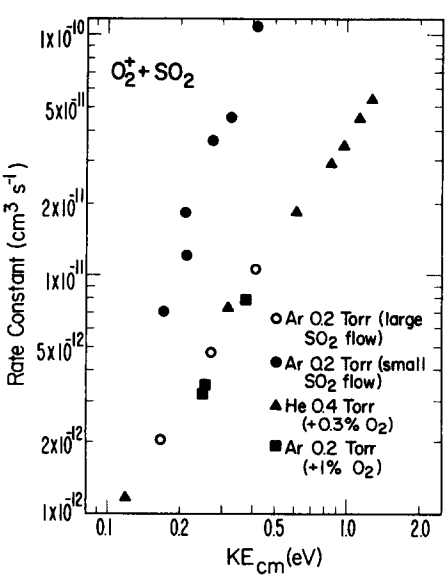

FIG. 5. Rate constant of the reaction $O_2^+ + SO_2$ as a function of kinetic energy in He and Ar buffers. In He the reactant ions are only O_2^+ ($v = 0$) due to quenching by CO_2. In the Ar buffer at energies above the threshold for vibrational excitation (~0.12 eV) two reaction rate constants for the limiting conditions of very small and very large SO_2 flows are given (see k_a and k_b in Fig. 9, respectively).

The quenching rate constant k_{q1} of O_2^+ ($v = 1$) by SO_2 has been measured at near thermal energy by the modified monitor ion technique using Xe as monitor gas. The result of the measurement is shown in Fig. 2. A quenching rate constant of $k_{q1} = 5.7(-10)$ cm^3 s^{-1} has been deduced from these data.

The results in Fig. 3 can now be explained in the following way: The fast reacting species at thermal energy are mostly O_2^+ ($v \geq 2$) ions. The endothermic charge transfer reaction of O_2^+ ($v = 1$) is certainly slower at thermal energy than the quenching and contributes only to a very small degree to the observed rapidly reacting ions. In a similar case, the endothermic charge transfer reaction of O_2^+ ($v = 0$) + Xe ($\Delta H = +0.06$ eV) has a reaction rate constant of $6(-11)$ cm^3 s^{-1} at thermal energy.[5] When the kinetic energy is increased, however, the quenching rate constant k_{q1} is expected to decrease while the reaction rate constant for O_2^+ ($v = 1$) increases, which results in an increasing fraction of O_2^+ ($v = 1$) ions that contribute to the fast reacting species as shown in Fig. 3.

In an Ar buffer at energies above 0.15 eV, the O_2^+ ion signal does not decline exponentially as a function of SO_2 flow. Instead, a curvature is observed on a semilogarithmic plot at low flows and a straight line observed only for large reactant gas flows. The rate constant that corresponds to this final exponential decline is exactly the same as the ground state rate constant for the same kinetic energy. This indicates that for these large reactant gas flows (0.5%–3% of the buffer flow) the vibrationally excited ions are more rapidly depleted by quenching and reaction than the vibrational state distribution can be reestablished by collisional excitation. This effect will be discussed in more detail for the $O_2^+ + CH_4$ reaction. The rate constants in an Ar buffer for the final decline of the primary ion signal and for the limiting case, of very small SO_2 flow (designated k_b and k_a, respectively, for the case of $O_2^+ + CH_4$) are given in Fig. 5 as a function of kinetic energy. The rate constant k_a for very small SO_2 flows should be the rate constant averaged over a vibrational state distribution given by the temperature T_i since the excitation of O_2^+ is mostly determined by collisions with the Ar buffer.

If the final exponential decline is extrapolated back to zero flow, one obtains the ratio of fast and slow reacting ions similar to the case in a He buffer. The fraction of fast reacting ions is given as a function of kinetic energy in Fig. 3. Also shown are the fractions of O_2^+ ions that are expected to be in the vibrationally excited states $v \geq 1$ and $v \geq 2$ for the given internal temperature T_i, assuming a Boltzmann distribution. One expects that the fraction of fast reacting ions is roughly proportional to the concentration of the excited states of O_2^+ that can react fast. The proportionality factor depends on the rate at which the excited states can be repopulated. Small deviations from proportionality are expected because the residence time and the excitation rate change with kinetic energy. Figure 3 shows that the fraction of fast reacting ions follows the curve for the fraction of O_2^+ ($v \geq 2$) ions for low kinetic energy. This is consistent with the results in a He buffer at near thermal energy where only O_2^+ ($v \geq 2$) ions were found to react rapidly. At an energy of 0.3–0.4 eV,

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TABLE I. Measured reaction rate constants of the fast reacting O_2^+ species k^*, the ground state O_2^+ ions k_g, the fraction of fast reacting O_2^+ ions B/A + B, quenching rate constants for $O_2^+(v=1)$ k_{q1}, and collision rate constants k_c for the ion-neutral pair at thermal energy.

Reactant neutral	k^* [$cm^3\ s^{-1}$]	k_g	B/A + B	k_{q1}	k_c
SO_2	1.2(−9)[a]	<1(−12)	0.22	5.7(−10)	1.2(−9)[b]
H_2O	1.35(−9)	<1(−12)	0.11	1.2(−9)	1.4(−9)
CH_4	7(−10)	5(−12)	0.25	6(−10)	1.14(−9)

[a] $a(-b) = a\times10^{-b}$.
[b] See Ref. 5 for calculation of k_c.

a transition is observed indicating that O_2^+ ($v=1$) ions also begin to react rapidly. This is probably a consequence of the fact that, at energies above about 0.35 eV, O_2^+ ($v=1$) reacts faster than it is quenched by SO_2.

The fact that vibrationally relaxed O_2^+ ions (with large SO_2 flow) have the same charge-transfer rate constant with SO_2 as O_2^+ ions in He proves that there is no rotational enhancement of the charge-transfer rate constant since the rotational temperature is very much higher in the Ar than in the He buffer. This result was found earlier for N_2O^+ charge transfer with NO.[4]

The rate coefficients measured at thermal energy for this system are summarized in Table I. The uncertainties in the measurements are estimated to be the following: k_g was measured with the standard accuracy of the technique (±30%). The accuracy was estimated to be (+60%/−40%) for k^* and k_b, (+80%/−50%) for k_a, and (+75%/−40%)[5] for k_{q1}.

B. $O_2^+ + H_2O$

H_2O reacts exothermically only with O_2^+ ($v\geq3$) ions by charge transfer. 11% ± 2% of the O_2^+ ions in the given state distribution in the FDT have been found to react fast with a rate constant k^* of 1.35(−9) $cm^3\ s^{-1}$. The quenching rate constant for O_2^+ ($v=1$) by H_2O has been determined by the Xe^+ monitor ion technique to be $k_{q1} = 1.2(-9)\ cm^3\ s^{-1}$.

C. $O_2^+ + CH_4$

In this reaction, three different channels are observed, two of them are endothermic for O_2^+ ($v=0$) and become exothermic for O_2^+ ($v=2$) and O_2^+ ($v=3$). This, added to the fact that the quenching rate constant of O_2^+ ($v\geq1$) by CH_4 is one-half Langevin,[5] makes it a very complicated reaction and, at the same time, a good candidate for the study of competition between reactive and quenching collisional processes. Among six possible exothermic channels only reaction (3) is observed, leading to the formation of the $CH_3O_2^+$ ion

$$O_2^+ + CH_4 \rightarrow CH_3O_2^+ + H + 4.8\ eV, \quad (3)$$
$$\rightarrow H_3O^+ + HCO + 4.9\ eV, \quad (4)$$
$$\rightarrow H_2O^+ + H_2CO + 2.3\ eV, \quad (5)$$
$$\rightarrow H_2CO^+ + H_2O + 4.1\ eV, \quad (6)$$
$$\rightarrow HCO^+ + H + H_2O + 3.1\ eV, \quad (7)$$
$$\rightarrow CH_3O^+ + OH + 3.4\ eV. \quad (8)$$

Two endothermic product channels for O_2^+ ($v=0$) are also observed:

$$O_2^+ + CH_4 \rightarrow CH_3^+ + HO_2 - 0.24(+0.04, -0.02)\ eV \quad (9)$$

which becomes exothermic by 0.22 eV for O_2^+ ($v=2$) and

$$O_2^+ + CH_4 \rightarrow CH_4^+ + O_2 - 0.6\ eV \quad (10)$$

which is exothermic by 0.09 eV for O_2^+ ($v=3$).

The thermochemical data are taken from Refs. 15–17 and the heat of formation of HO_2 from Ref. 18.

The product ions CH_3^+ and CH_4^+ react rapidly with CH_4,[19]

$$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2, \quad k = 1.2(-9)\ cm^3\ s^{-1}, \quad (11)$$

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3, \quad k = 1.2(-9)\ cm^3\ s^{-1}. \quad (12)$$

CH_3^+ and CH_4^+ are therefore only intermediate species with very small abundances and their production is monitored by the ion signals of $C_2H_5^+$ and CH_5^+.

The structure of the product ion $CH_3O_2^+$ is protonated formic acid, i.e., $HC(OH)_2^+$, whose heat of formation[17] is 97.2 kcal mol^{-1}. The structure has been established by Lindinger and his colleagues[20,21] in two different kinds of experiments. Isotopic exchange with D_2O has been measured for the $CH_3O_2^+$ product of reaction (3) and for $CH_3O_2^+$ produced by reaction of formic acid ion with formic acid with identical results, namely the two OH hydrogen atoms are successively exchanged while the CH hydrogen is not.[20] Also, collisional breakup of the $CH_3O_2^+$ ions produced both ways gives identical results[21]; the ions H_3O^+ and HCO^+ are produced in comparable abundance at all kinetic energies sufficient for breakup.

The energy dependence of the individual rate constants of the reaction channels (3), (9), and (10) and of the overall reaction rate constant for O_2^+ ($v=0$) ions in He buffer is shown in Fig. 6. These measurements were performed using the electron impact ion source immersed in the flow tube and adding enough O_2 so that all primary ions were quenched to the ground vibrational state by O_2^+–O_2 collisions. The measurements were also repeated with the mass-selected ion

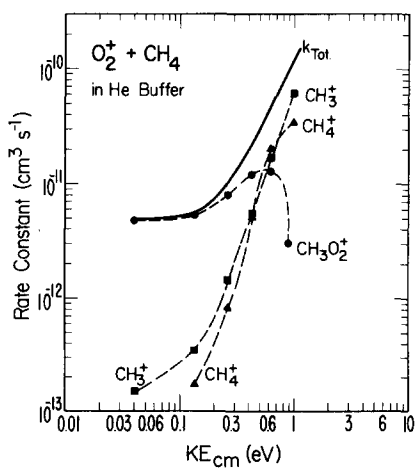

FIG. 6. Rate constants for the three individual reaction channels in the reaction of $O_2^+(v=0)$ with CH_4 as a function of kinetic energy in the He buffer.

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source and the contribution of the fast reacting excited ion species to the three product channels was subtracted from the ion signals. The results of both measurements were identical.

Figure 6 shows that the steep increase of the reaction rate constant for O_2^+ ($v = 0$) + CH_4 above about 0.15 eV is mainly due to the opening of the two endothermic reaction channels (9) and (10). The small CH_3^+ and CH_4^+ signals at low energy are consistent with the endothermicities of reaction channels (9) and (10). The CH_3^+ signal at 0.04 eV (3/2 $k_B T$) corresponds to a rate constant $\sim 1(-13)$ cm^3 s^{-1}, about 10^{-4} of the collision rate constant. The Boltzmann factor $\exp(-0.24/k_B T)$ is also near 10^{-4}. The CH_4^+ channel has an equivalent $1(-13)$ cm^3 s^{-1} rate constant near 0.1 eV, or 2.5 times higher than the CH_3^+ value, corresponding to the ~ 2.5 time greater activation energy, or ~ 0.6 eV.

When the O_2^+ ions in the given vibrational state distribution (65% in $v \geqslant 1$, 22% in $v \geqslant 2$, and 11% in $v \geqslant 3$) produced in the mass selected ion source are reacted with CH_4, one observes that $\sim 24 \pm 2\%$ of the O_2^+ ions undergo a very rapid reaction, as shown in Fig. 4, with a rate constant $k^* = 7(-10)$ cm^3 s^{-1}. This fraction, almost identical to that reacting rapidly with SO_2, must be almost exclusively the O_2^+ ions in $v \geqslant 2$. The reaction rate constant of the slowly reacting ions is identical to the rate constant for O_2^+ ($v = 0$) ions, $k_g = 5(-12)$ cm^3 s^{-1} obtained from measurements where the O_2^+ ions were vibrationally relaxed by O_2 collisions prior to the reaction. This is already an indication that the population of O_2^+ ($v = 1$) is very rapidly relaxed by CH_4.

The branching ratio of the three reaction channels for the fast reacting ions can be determined from the results shown in Fig. 7:

$$\begin{aligned} O_2^+ (v \geqslant 2) + CH_4 &\rightarrow CH_4^+ + O_2 \quad 52\%, \\ &\rightarrow CH_3^+ + HO_2 \quad 37\%, \\ &\rightarrow CH_3O_2^+ + H \quad 11\%. \end{aligned}$$

From these percentages, one can calculate that for the whole population of O_2^+ ions, $12.5 \pm 2\%$ react to give CH_4^+. For this reaction channel, O_2^+ ($v \geqslant 3$) are required, the abundance of which is about 11%. This leads to the conclusion that all the O_2^+ ($v \geqslant 3$) ions react by charge transfer with CH_4. The $11.5 \pm 2\%$ of the whole population of O_2^+ given CH_3^+ and $CH_3O_2^+$ are therefore all the O_2^+ in $v = 2$.

The absence of the contribution of O_2^+ ($v = 1$) to the endothermic production of CH_3^+ is consistent with the fact that the O_2^+ ($v = 1$) are more rapidly quenched than they react at thermal energy. This is shown by the results in Fig. 1 obtained with the Xe^+ monitor ion technique. The recovery of the O_2^+ ion signal with CH_4 gas flow at a fixed monitor gas flow indicates that the current of ground state ions reaching the monitor gas inlet increases. The quenching rate constant k_{q1} obtained from fitting model calculations to the measured results is $6(-10)$ cm^3 s^{-1}.

When, in a different experimental approach, the products CH_3^+ and CH_4^+ from the $O_2^+ + CH_4$ reaction were used as monitor ions to study the quenching of vibrationally excited O_2^+ ions with CO_2 and Kr, the values $k_q(CO_2) = 2.1(-10)$ cm^3 s^{-1} and $k_q(Kr) = 1.6(-11)$ 10^{-11} cm^3 s^{-1} were obtained. The values were thus almost identical for both monitor ions. These values are in very good agreement with the results obtained[5,6] with the SO_2^+ monitor ion technique $k_{q2}(CO_2) = 2(-10)$ cm^3 s^{-1} and $k_{q2}(Kr) = 1.7(-11)$ cm^3 s^{-1}. This confirms the conclusion that at room temperature the product ions CH_3^+ and CH_4^+ are primarily due to O_2^+ ($v \geqslant 2$) ions. One would expect that the quenching rate constant observed with the CH_4^+ monitor ions would be higher than k_{q2} because it should essentially give k_{q3}, but the experimental technique may not be accurate enough to resolve the small difference between k_{q2} and k_{q3} in this case.

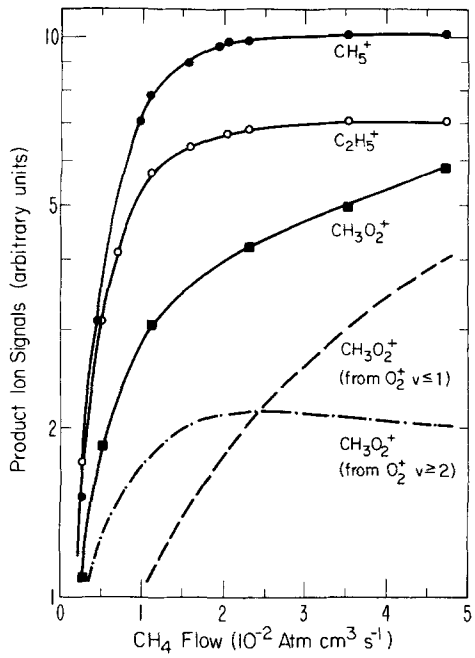

FIG. 7. Ion signals of the product ions from reaction O_2^+ (v) + CH_4 as a function of CH_4 flow in the He buffer. The curve $CH_3O_2^+$ [from O_2^+ ($v<1$)] is calculated from the known ground state reaction rate constant k_g and the relative concentration of O_2^+ ($v = 0,1$) ions. The curve $CH_3O_2^+$ [from O_2^+ ($v \geqslant 2$)] is obtained by subtraction of $CH_3O_2^+$ from O_2^+ ($v<1$) from the total $CH_3O_2^+$ curve. The branching ratio of the three product channels CH_3^+, CH_4^+, and $CH_3O_2^+$ in the reaction O_2^+ ($v \geqslant 2$) + CH_4 is obtained from these data.

Figure 8 summarizes the results of reaction rate constant measurements as a function of kinetic energy in the different buffer gases He, Ne, and Ar. In a Ne buffer, about 24% of the O_2^+ ions reacted rapidly just as in the case of a He buffer, indicating that the vibrationally excited ions produced in the ion source are not quenched in the FDT in agreement with the earlier observations.[5,6] The rate constants given for He and Ne buffer gases are those of the slowly reacting ground state O_2^+ ions. The rate constants in He and Ne are identical within the experimental error limit over the entire energy range. This implies that the O_2^+ ions are not vibrationally excited in Ne. This differs from the observations of Alge *et al.*[3] who found a rate constant enhancement in Ne. In order to further demonstrate that there is no significant excitation of O_2^+ in Ne buffer at high kinetic energy in the FDT, 2% of O_2 gas was added to the buffer which should result in a very efficient quenching of vibrational excitation. No change in the rate constant of the slowly react-

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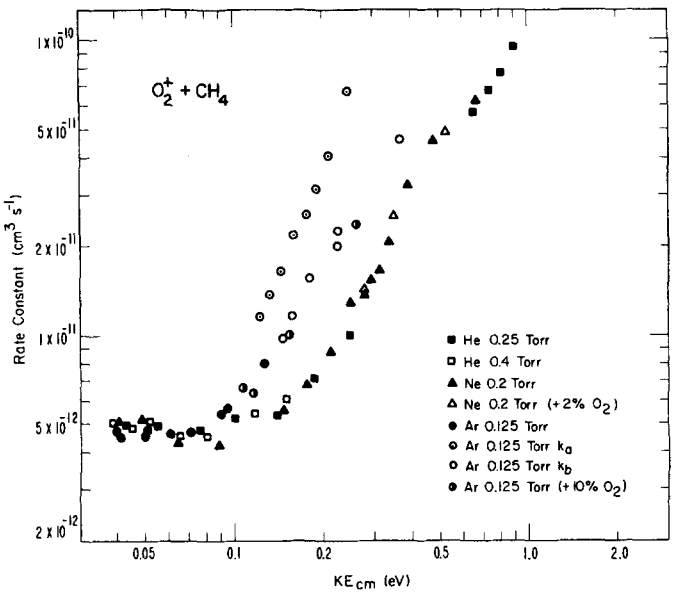

FIG. 8. Rate constant of the reaction $O_2^+ + CH_4$ as a function of kinetic energy in He, Ne, and Ar buffers. The reaction rate constants in pure He and Ne buffers are those for the ground state ion k_g. For the Ar buffer at energies above the threshold for vibrational excitation of O_2^+ ($\sim$0.12 eV), two rate constants k_a and k_b, for small and large CH_4 flows, have been determined (see Fig. 9). In some measurements in the Ne and Ar buffers, O_2 has been added to quench the vibrational excitation of the O_2^+ ions.

ing ions was observed while the fast reacting ions disappeared.

In an Ar buffer, where excitation of the O_2^+ ions in the FDT is possible at sufficiently high kinetic energy, a curvature appears above 0.12 eV in the decline of the logarithm of the ion signal as a function of CH_4 flow. A typical example of a measurement at 0.23 eV is shown in Fig. 9 (the reaction rate constants given in Fig. 8 for Ar buffer at KE cm > 0.12 eV are those for the limiting cases of very small and very large flows of CH_4, k_a, and k_b, respectively). The observation of a change in the slope of the decline is similar to the behavior of the reaction $O_2^+ + SO_2$ in an Ar buffer. The two cases differ

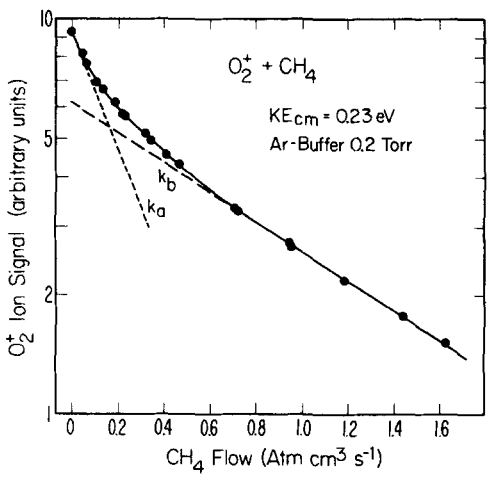

FIG. 9. Typical result in the measurement of the rate constants for the reaction $O_2^+ + CH_4$ in the Ar buffer at energies above the threshold for vibrational excitation of O_2^+ ($\sim$0.12 eV). No unique rate constant can be obtained but rate constants for the limiting conditions of very small and very large CH_4 flows, k_a and k_b, respectively, have been deduced.

however. For $O_2^+ + SO_2$, the rate constant for large SO_2 flow coincides with the ground state rate constant measured in He buffer while for $O_2^+ + CH_4$ the rate constants for large CH_4 flow in Ar is still significantly higher than the ground state rate constant. When 10% O_2 gas is added to the Ar buffer to quench the vibrationally excited O_2^+ ions, the curvature in the primary ion decay disappears for the reaction $O_2^+ + CH_4$ and the unique rate constant derived is identical to that for large CH_4 flows (as shown in Fig. 8).

The change of the reactivity of O_2^+ as a function of reactant gas addition in the case of the reactions $O_2^+ + SO_2$ and $O_2^+ + CH_4$ in an Ar buffer at high kinetic energy can be understood in the following way: The quenching rate constants measured for the deactivation of O_2^{+*} by SO_2 and CH_4 are about $k_{q1} = 6(-10)$ cm^3 s^{-1} while the quenching rate constant for Ar is only $1(-12)$ cm^3 s^{-1} at thermal energy.[5,6] From detailed balance, one expects that the excitation rate constants have the same order of magnitude at kinetic energies above the excitation threshold as the quenching rate constants. More precisely, both rate constants should decrease somewhat with increasing kinetic energy (not more than an order of magnitude) as expected from the quenching studies.[5,6] Since relaxation and excitation by CH_4 and SO_2 is about 600 times faster than by the Ar buffer, one expects that the internal temperature of the O_2^+ ions in the FDT is controlled almost exclusively by the collisions with CH_4 and SO_2 when these gases are added to the buffer in mixing ratios larger than 1%. In the case of CH_4, the internal temperature of O_2^+ is expected to decrease because of the light mass of CH_4 compared to Ar and also because of the ability of the buffer to store internal energy. Inelastic collisions resulting in excitation transfer to the buffer have been found by Viehland and Fahey[22] to lower the kinetic energy of the ions and, similarly, one expects that the internal energy of the molecular ion is decreased compared to the value calculated from Eq. (1). It is surprising, that for large SO_2 addition, the O_2^+ ions show a reactivity as if they were all quenched to the ground state. For the large mass of SO_2 one would expect a larger degree of excitation than for the case of CH_4. One possible explanation is that V–V transfer occurs in this case so that detailed balancing does not apply under drift tube conditions, i.e., vibrational deexcitation is much faster than excitation. For example, the two quantum excitations of SO_2,

$$O_2^+ (v = 1) + SO_2(000) \rightarrow O_2^+ (v = 0) + SO_2(101), \quad (13)$$

must be nearly resonant, since $h\nu[SO_2(100)] + h\nu[SO_2(001)] - h\nu[O_2^+ (v = 1)] = 9$ cm^{-1}.

Small differences in the rate constants of ion–molecule reactions in different buffer gases can occur due to differing speed distributions of the drifting primary ions. This has been demonstrated[23] for the reaction $O^+ + N_2$ which shows an extremely steep increase of the rate constant with kinetic energy. For the reaction $O_2^+ + Xe$[5,6] and also for $O_2^+ + SO_2$ with large addition of SO_2, no differences are observed in the rate constants obtained in He and Ar buffer gases. Therefore, one does not expect that the difference in speed distributions causes a significant effect in the reaction O_2^+

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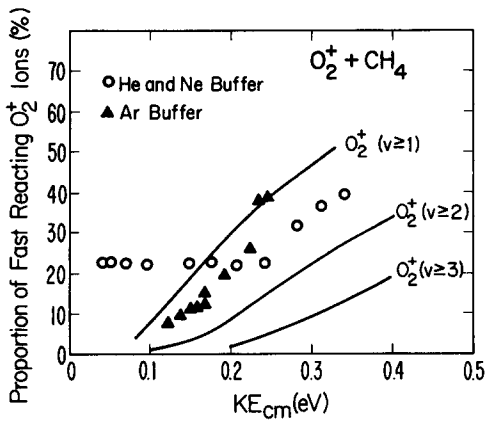

FIG. 10. Fraction of $O_2^+(v)$ ions reacting fast with CH_4 as a function of the ion-reactant center-of-mass kinetic energy KE_{cm}^R, in He, Ne, and Ar buffer gases. In He and Ne, the vibrational state distribution of the O_2^+ ions is equal to that prior to injection into the flow tube (see the text). In an Ar buffer, the vibrational state distribution is determined by exciting and deexciting collisions of O_2^+ with the buffer. The distribution calculated for steady state is shown in the figure for comparison.

$+ CH_4$, which shows less variability of the rate constant with energy than the reaction $O^+ + N_2$.

The fraction of O_2^+ ions reacting fast with CH_4 in an Ar buffer can be found in the same way as for the SO_2 reaction. Figure 10 shows the percentage of rapidly reacting O_2^+ as a function of kinetic energy along with the fractions of O_2^+ ions expected to be in the excited states O_2^+ ($v>1$), O_2^+ ($v>2$), and O_2^+ ($v>3$) for the corresponding excitation temperature T_i. The data indicate that below 0.25 eV the fast reacting ions are mainly O_2^+ ($v>2$) ions while above 0.25 eV, O_2^+ ($v=1$) ions also react rapidly.

The present vibrational quenching data combined with other recent data on the $O_2^+ + CH_4$ reaction, yield a rather detailed picture of the reaction mechanism. The vibrational quenching rate constant $k_{q1} = 6(-10)$ cm^3 s^{-1} allows an estimate of the $[O_2^+ \cdot CH_4]^*$ collision complex lifetime. The rate of vibrational predissociation of the complexes

$$[O_2^+(v=1)\cdot X]^* \xrightarrow{k_{vp}} O_2^+(v=0) + X \tag{14}$$

are found to be $k_{vp} \sim 10^9$ s^{-1} for X = Ar, N_2, CO_2, H_2O, and SO_2 and for $NO^+(v)$ vibrational predissociation by CO_2, CH_4, NH_3, and CO.[24,25] These values are derived from the expression $k_{vp} = k_q k_s / k^3$, where k_q is the experimental vibrational quenching rate constant, k^3 is the experimental three-body association rate constant for

$$O_2^+ + X + M \xrightarrow{k^3} O_2^+ \cdot X + M, \tag{15}$$

and k_s is the stabilization rate constant for

$$[O_2^+ \cdot X]^* + M \xrightarrow{k_s} O_2^+ \cdot X + M, \tag{16}$$

assumed to be the collision rate constant $k_s = k_c = 2\pi e(\alpha/\mu)^{1/2}$ for heavy M≠He. The relation $k_{vp} = k_q k_s / k^3$ is valid for the cases where vibrational quenching is slow, i.e., $k_q < k_c$, otherwise vibrational quenching is rate limited by the complex formation step and the derived value of k_{vp} is only a lower limit. Since O_2^+ ($v=1$) is quenched in about half the collisions with CH_4 (Table I), it appears that the complex lifetime is comparable to the reciprocal vibrational predissociation rate $k_{vp}^{-1} \sim 1(-9)$ s. This is a longer lifetime than one would expect from purely electrostatic bond considerations. For example, the lifetime τ of the NO^+–CH_4 complex can be estimated to be $\sim 3(-11)$ s at 300 K from $k^3 = k_1 k_s \tau$. The complex formation rate constant and the collisional stabilization rate constant are assumed to be Langevin and the $NO^+ + CH_4 + M \rightarrow NO^+ \cdot CH_4$ three-body rate constant[26] is $k^3 \leqslant 2(-29)$ cm^6 s^1 in a He/N_2 = 2.25 gas mixture at 300 K.

The mechanism leading to a longer lifetime for $O_2^+ \cdot CH_4$ complex is believed to be H^- abstraction to form $CH_3^+ \cdot HO_2$ in the complex. This is the 0.24 eV endothermic reaction (4) except that the HO_2 (with a very large dipole moment of 2 D) is trapped and cannot separate at thermal energy. The electrostatic attraction energy is quite enough to supply this 0.24 eV at impact. This is analogous to the situation recently described in which Si^+ was found to have an anomalously large three-body association with O_2 by virtue of the slightly endothermic formation of SiO^+ in an $[SiO^+ \cdots O]^*$ complex which allows Si^+ access to the deep potential well between the oxygen atoms.[27] That hydride ion (H^-) abstraction occurs is evident from the steep onset of CH_3^+ production at threshold shown in Fig. 6. Hydride ion abstractions as a class are very often efficient so this is not an unexpected result. The hydride ion abstraction first step in reaction (3) aids greatly in terms of reaction dynamics as well. The reaction of O_2^+ with CH_4 to produce protonated formic acid is a remarkable one, involving the breaking of the O–O bond and three C–H bonds with the formation of two C–O and two O–H bonds. The initial H^- abstraction lowers the O–O bond strength from 6.7 eV in O_2^+ to 2.6 eV in HO_2, as well as breaking one C–H bond and making one O–H bond. Since the reaction probability for reaction (3) is $\sim 5(-3)$, the ratio of k_g to k_c in Table I, the lifetime of the $[O_2^+ \cdot CH_4]^*$ (or $[CH_3^+ \cdot HO_2]^*$) complex against reaction to produce $CH_3O_2^+ + H$, must be $\sim \tau/P \sim 5(-10)/5(-3) \sim 1(-7)$ s.

A recent experiment which beautifully confirms this picture is the measurement of reaction (3) down to 20 K in a uniform supersonic jet at Meudon, and confirmed down to 70 K by flow-drift tube measurements at Birmingham.[28] The value of k_g increases with decreasing temperature, following a very linear $T^{-1.8}$ dependence from ~ 150 down to 20 K. At 20 K the rate constant is $5(-10)$ cm^3 s^{-1}, almost half of $k_c = 1.14(-9)$ cm^{-3} s^{-1}. A smooth extrapolation on a linear T scale yields almost exactly k_c at 0 K. This is qualitatively quite consistent. The lifetime will increase with decreasing T and at 20 K will be $\tau(20\text{ K}) \sim \tau(300\text{ K})\left(\frac{300}{20}\right)^{1.8} \approx 1(-7)$ s. This is comparable to the lifetime for $CH_3O_2^+$ production [i.e., reaction (3)] so that reaction should occur on $\sim 1/2$ the collisions as observed.

An interesting observation is that the reaction

$$O_2^+ \cdot O_2 + CH_4 \rightarrow O_2^+ \cdot CH_4 + O_2 \tag{17}$$

has been observed,[29,30] i.e., a stable $O_2^+ \cdot CH_4$ cluster ion exists in spite of the fact that O_2^+ reacts with CH_4. However, the reaction scheme we have suggested above requires that the O_2^+ and CH_4 collide with the 0.24 eV energy necessary

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for hydride ion abstraction by the O_2^+. Evidently when the CH_4 is "gently" inserted in the switching reaction (17), the endothermic hydride ion abstraction cannot occur and therefore the subsequent $CH_3O_2^+$ production on $\sim 1(-7)$ s time scale also does not occur.

IV. SUMMARY AND CONCLUSIONS

For the reactions $O_2^+ + SO_2$, $O_2^+ + CH_4$, and $O_2^+ + H_2O$, very fast quenching of the first vibrationally excited state of O_2^+ was found while reaction of this state was very slow at thermal energy. Only at higher kinetic energy does the reactive channel become dominant in the reactions of O_2^+ ($v = 1$) with SO_2 and CH_4. In the absence of reaction, one would expect that the vibrational states O_2^+ ($v = 2$) and O_2^+ ($v = 3$) would be even more efficiently quenched by SO_2 or CH_4 than is O_2^+ ($v = 1$). For the higher vibrational levels however, the quenching process is in competition with exothermic reaction channels. For these states it is observed that reactive processes occur at almost the collision rate and dominate the quenching.

In the reaction $O_2^+ + CH_4$, the two endothermic reaction channels leading to CH_3^+ and CH_4^+ become dominant at higher kinetic energy ($\gtrsim 0.5$ eV) and at higher internal energy ($v > 2$) of the O_2^+ ions. Quite similar observations have been made by Tanaka *et al.*[31] who used an experimental technique in which the O_2^+ ions can be prepared in the selected vibrational states $v = 0$, 1, and 2.

In the reaction studies in an Ar buffer at higher kinetic energies, the steady state of vibrational excitation and deexcitation of O_2^+ is mainly controlled by the reactant gases CH_4 and SO_2 when they are added to the buffer in quantities larger than a few tenths of a percent. It is not possible to predict the steady-state internal temperature of O_2^+ in this case because T_i depends on the degree to which collisional energy and vibrational energy of O_2^+ are transferred into the internal modes of the molecular targets during collisions.

The combination of the present $O_2^+(v)$ vibrational quenching and reaction studies with CH_4, recent very low temperature measurements of the reaction rate constant, and collisional breakup studies and isotopic exchange studies of the $CH_3O_2^+$ product ion, allow a rather detailed insight into the reaction mechanism. This also involves the recently developed information about the systematics of vibrational relaxation of diatomic ions with neutrals. It is clear that the newly developing field of molecular ion vibrational relaxation studies will provide useful insight into reaction dynamics, just as neutral vibrational relaxation studies have done for several decades.

APPENDIX

The modified monitor ion technique that is used to measure the quenching rate constants for the lower vibrational levels of O_2^+ when the upper states react with the quenching gas is demonstrated here for the simplified case of a three-state model.

$[A^+(0)]_0$, $[A^+(1)]_0$, and $[A^+(2)]_0$ are the initial concentrations at the upstream end of the FDT of the ground state ions, the excited, unreactive ions, and the excited, reactive ions, respectively. (Refer to Fig. 11.) With Q as the quenching/reactant gas, we have

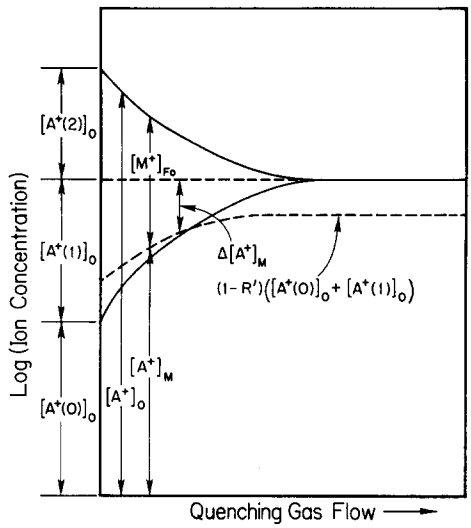

FIG. 11. Plot of ion concentrations as a function of quenching/reactant gas for the three-state system analyzed in Appendix A. $[A^+(n)]_0$, $n = 0, 1, 2$, are the initial concentrations for the three states of the primary ion A^+. $[A^+]_M$ and $[A^+]_0$ are the concentrations of all A^+ ions at the FDT detector with and without monitor gas M added to the system. $[M^+]_{F_0}$ is the monitor ion concentration at the detector. $\Delta[A^+]_M$ is a difference concentration that is used to give the quenching rate of $A^+(1)$ ions when R is close to unity (see the Appendix).

$$A^+(0) + Q \rightarrow \text{no reaction}, \tag{A1}$$

$$A^+(1) + Q \xrightarrow{k_q} A^+(0) + Q, \tag{A2}$$

$$A^+(2) + Q \xrightarrow{k_r} \text{products}. \tag{A3}$$

$[A^+]_0$ is the initial primary ion concentration that includes all states of the ion

$$[A^+]_0 = [A^+(0)]_0 + [A^+(1)]_0 + [A^+(2)]_0. \tag{A4}$$

The concentration of A^+ ions in the flow tube is a function of the flow of quenching/reactant gas Q and the rate constants of Eqs. (A2) and (A3). We have then

$$[A^+] = [A^+(0)]_0 + [A^+(1)]_0 + [A^+(2)]_0 \exp(-\alpha\tau), \tag{A5}$$

$$[A^+(0)] = [A^+(0)]_0 + [A^+(1)]_0(1 - \exp(-\beta\tau)), \tag{A6}$$

where $\alpha = k_r[Q]$, $\beta = k_q[Q]$, and τ is the residence time of the ions in the drift-reaction region.

The monitor ion signal M^+ is produced from A^+ ions reacting with the monitor gas M. Both the excited state and ground state ions will, in general, react to produce M^+ ions. The fractions of excited state and ground state ions that react to produce M^+ are a function of the respective reaction rate constants with M and the flow of M. These fractions are designated R and R', respectively, at a monitor flow F_0 [see Eqs. (A5) and (A6) in Ref. 5]. The concentrations of M^+ ions at the FDT detector is given by

$$[M^+]_{F_0} = R([A^+] - [A^+(0)]) + R'[A^+(0)], \tag{A7}$$

where the A^+ concentrations are evaluated at the monitor gas inlet. Substituting Eqs. (A5) and (A6) in Eq. (A7), we obtain

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$$[M^+]_{F_0} = [A^+(1)]_0((R - R')\exp(-\beta\tau) + R') + [A^+(2)]_0 R \exp(-\alpha\tau) + R'[A^+(0)]_0. \quad \text{(A8)}$$

The addition of monitor gas to the FDT results in a reduction of A^+ ions in the system. The concentration of A^+ ions at the detector with monitor gas present is given by

$$[A^+]_M = [A^+] - [M^+]_0. \quad \text{(A9)}$$

Using Eqs. (A5) and (A7), we have

$$[A^+]_M = [A^+(0)]_0(1 - R) + [A^+(1)]_0 \times (1 - R' - (R - R')\exp(-\beta\tau)) + [A^+(2)]_0(1 - R)\exp(-\alpha\tau). \quad \text{(A10)}$$

When the flow of Q is large, the exponential terms vanish and Eq. (A10) reduces to a constant term that depends only on the monitor flow F_0 through R and R':

$$[A^+]_M = [A^+(0)]_0(1 - R) + [A^+(1)]_0(1 - R'), \quad [Q] \text{ large.} \quad \text{(A11)}$$

The difference between Eqs. (A11) and (A10), therefore, is a term that depends on Q and is defined as $\Delta[A^+]_M$. We then have

$$\Delta[A^+]_M = [A^+(1)]_0(R - R')\exp(-\beta\tau) - [A^+(2)]_0(1 - R)\exp(-\alpha\tau). \quad \text{(A12)}$$

In summary, $\Delta[A^+]_M$ is the magnitude of the change in the A^+ ion signal in the FDT detection system as a function of Q for fixed values of R and R' set by the monitor gas M at flow F_0.

Finally, if the monitor gas flow is sufficiently large, R can be made to be approximately unity (see Appendix A, Ref. 5), causing the second term of Eq. (A12) to vanish. For this condition, the change in the A^+ ion signal is a pure exponential that depends only on the quenching rate constant k_q of $A^+(1)$ ions, the desired result.

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