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# Energy dependence of the O⁻ transfer reactions of $O_3^-$ and $CO_3^-$ with NO and SO₂

D. L. Albritton, I. Dotan,[a] G. E. Streit,[b] D. W. Fahey, F. C. Fehsenfeld, and E. E. Ferguson

*Aeronomy Laboratory, NOAA Environmental Research Laboratories, Boulder, Colorado 80303*

The O⁻ transfer reactions of $O_3^-$ and $CO_3^-$ with NO and SO₂ were measured as a function of temperature in the range 170–605 K in a variable-temperature flowing afterglow system and as a function of center-of-mass kinetic energy in the range 0.04–2 eV in a flow-drift tube system. The rate constant in each case showed a marked energy dependence. The rate constants measured as a function of temperature were essentially the same as those measured as a function of kinetic energy in He and Ar buffer gases when the comparison is made at the same mean center-of-mass kinetic energy. The results imply that the reactions have negligible vibrational or rotational energy dependence.

## I. INTRODUCTION

Reactions of negative ions are of interest in connection with the ion chemistry of planetary atmospheres, combustion systems, and gas discharges. The translational and internal energy dependences of ion–molecule reaction rate constants give an insight into the reaction mechanisms involved. To date, little such data has been obtained for negative ion reactions.

In the Aeronomy Laboratory, reaction rate constants are measured both in a variable temperature flowing afterglow (FA) system and in a flow drift tube (FDT) system. A comparison among the rate constants measured in the FA system and in different buffer gases in the FDT system provide information concerning the role of internal energy modes in the reaction process. For example, with He and Ar buffer gases in the FDT, large differences have been observed for reaction rate constants of positive ions measured as a function of center-of-mass collision energy.[1-4] The differences are interpreted to be the result of the enhancement of the reaction rate constant by ion vibrational excitation.

The level of excitation of the internal modes of the reactant ions is assumed to be given by steady state conditions in the ion/buffer gas collision complex.[5] This "steady state assumption" plays an important role in the interpretation of the present results. In general, sufficient information is not available to determine the validity of this assumption. Therefore, steady state must be considered to give an upper limit for the level of internal excitation. In one case, that of ions in a He buffer in the FDT, the results clearly indicate that the steady state assumption is not valid for ion vibrational modes. A further discussion of this assumption will be presented in a following section.

Various studies of the energy dependence of negative ion reactions have been made previously.[6-12] Of the flow tube studies,[6-10] only one[10] has utilized both a He

and Ar buffer gas to test the effect of internal excitation of a molecular ion. No effect was found in this study of the $O_3^- + CO_2$ reaction. Other studies include measurements of many negative ions reacting with O₃ in a tandem mass spectrometer[11] and reactions of SO⁻ and O⁻ in an ion source/mass spectrometer system.[12] In these types of studies, the effect of internal excitation can be explored in a limited manner by the use of apparatus temperature and the preparation of excited states by chemical reaction.

In the present study, several reaction rate constants of polyatomic negative ions were measured in the FA and FDT systems. Specifically, the rate constants of $O_3^-$ and $CO_3^-$ ions reacting with NO and SO₂ were measured as a function of center-of-mass kinetic energy in the range of 0.02–2 eV. The following sections provide details of the experimental apparatus, results of the measurements, and a discussion of the results.

## II. EXPERIMENTAL APPARATUS AND TECHNIQUE

The variable-temperature flowing afterglow (FA) system has been described in detail previously.[13,14] The measurements were made in a He buffer gas with a pressure near 0.4 Torr and in the temperature range of 170–605 K. Temperatures below 300 K were obtained by pulsing liquid nitrogen through cooling coils. Temperatures above 300 K were obtained with resistive heating elements attached to the flow tube. Temperature uniformity was monitored with a series of thermocouples placed along the length of the flow tube.

The flow-drift tube (FDT) system has been described in detail previously.[6,15] The measurements were made at several pressures in He and Ar buffer gases at a temperature of 300 K.

In both systems, ionization was produced by a heated, electron-emitting filament immersed in the buffer gas. The $O_3^-$ reactant ion was produced by two methods that have been described previously.[10] The first involved O⁻ production followed by three-body association with O₂. The second method involved the reaction of O⁻ and $O_2^-$ with O₃ to produce $O_3^-$. In both methods, the addition of CO₂ downstream from the electron gun converted $O_3^-$

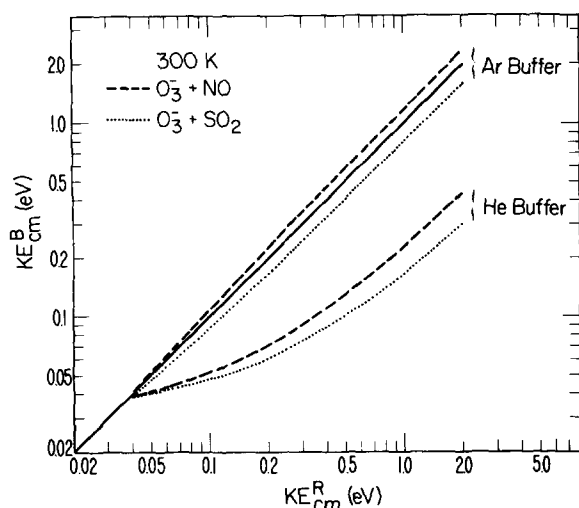0021-9606/83/116614-06$02.10    © 1983 American Institute of Physics

FIG. 1. $KE^B_{c.m.}$ vs $KE^R_{c.m.}$ for the reactions of $O_3^-$ with NO and $SO_2$ for steady state conditions. $KE^R_{c.m.}$ is the mean, center-of-mass kinetic energy between $O_3^-$ and the NO or $SO_2$ reactant molecule from Eq. (1). $KE^B_{c.m.}$ is the corresponding mean, center-of-mass kinetic energy between $O_3$ and the He or Ar buffer gas atom from Eq. (3). The dashed and dotted lines are the results for NO and $SO_2$, respectively, in the FDT system in a He and Ar buffer gas. The solid line, given by $KE^B_{c.m.}$ $=KE^R_{c.m.}$, applies for both reactions in the FA system.

ions to $CO_3^-$ ions.[10] The first method above was used primarily in the FA system. The second method was used primarily in the FDT system in order to avoid the addition of large amounts of $O_2$ that would change the transport properties of the reactant ions in the drift field.

In both systems, the rate constant was obtained by measuring the decline of the primary ion signal as a function of the absolute addition rate of the neutral reactant to the flow tube.[14,15] In the FA system, rate constant measurements were made as a function of the flow tube temperature $T$. In the FDT system, rate constant measurements were made at a flow tube temperature of 300 K as a function of $E/N$ where $E$ is the electric field strength in the flow tube and $N$ is the buffer gas number density.

In both systems, the rate constant results are expressed as a function of the mean, center-of-mass kinetic energy $KE^R_{c.m.}$, of the ion/reactant neutral pair. In the FA, $KE^R_{c.m.} = \frac{3}{2}k_B T$ where $k_B$ is Boltzmann's constant. In the FDT, values of $E/N$ were converted into values of $KE^R_{c.m.}$ by [15]

$$KE^R_{c.m.} = \frac{3}{2}k_B T + \frac{1}{2}v_d^2 M_R\left(\frac{m + M_B}{m + M_R}\right), \qquad (1)$$

$$v_d = \mu E , \qquad (2)$$

where $v_d$ is the ion drift velocity, $\mu$ is the ion mobility, $M_R$ is the mass of the neutral reactant, $M_B$ is the mass of the buffer gas, and $m$ is the mass of the reactant ion. Equation (1) has been shown experimentally[15] and theoretically[16-18] to yield an accurate mean energy for atomic ion-neutral combinations.

The ion internal temperature $T_i$ in steady state is given by the ion/buffer gas mean, center-of-mass kinetic energy $KE^B_{c.m.}$, through $\frac{3}{2}k_B T_i = KE^B_{c.m.}$.[5] In the FA, the relation $KE^B_{c.m.} = KE^R_{c.m.}$ holds in steady state. In the FDT, $KE^B_{c.m.}$ is given by Eq. (1) with $M_R = M_B$ as

$$KE^B_{c.m.} = \frac{3}{2}k_B T + \frac{1}{2}M_B v_d^2 . \qquad (3)$$

Figure 1 shows the correspondence between $KE^B_{c.m.}$ and $KE^R_{c.m.}$ for $O_3^-$ ions with NO and $SO_2$. The correspondence for $CO_3^-$ ions with NO and $SO_2$ is nearly identical to that for $O_3^-$ ions. The results show that the ion internal temperature in the FA is approximately equal to that in an Ar buffer in the FDT while the temperature in a He buffer in the FDT is substantially lower at the higher values of $KE^R_{c.m.}$.

The flow of neutral reactants, NO and $CO_2$, was controlled by a viscous flow system.[14] High-purity cylinders of NO and $CO_2$ were obtained commercially. NO was further purified in a silica gel trap held at $-80\,°C$ in a dry ice–ethanol bath. After trapping, the remaining reactive nitrogen impurities were estimated to be less than 0.1%.

## III. RESULTS AND DISCUSSION

The rate constant data are shown in Figs. 2–5 where the rate constant k is plotted as a function of $KE^R_{c.m.}$ in the range 0.02–2.0 eV. Each figure includes data from the FA system and data from the FDT system for both He and Ar buffer gases at two different pressures. The rate constants obtained from the two measurement techniques at thermal energy, i.e., $KE^R_{c.m.} = 0.04$ eV, are included in Table I along with the collision rate constants $k_c$. The collision rate constants follow from the variational calculations of Chesnavich *et al.*[19] at low energies. The variational calculations result in a modification of the usual Langevin collision rate constant for the case of a polar neutral reactant. The absolute uncertainty in
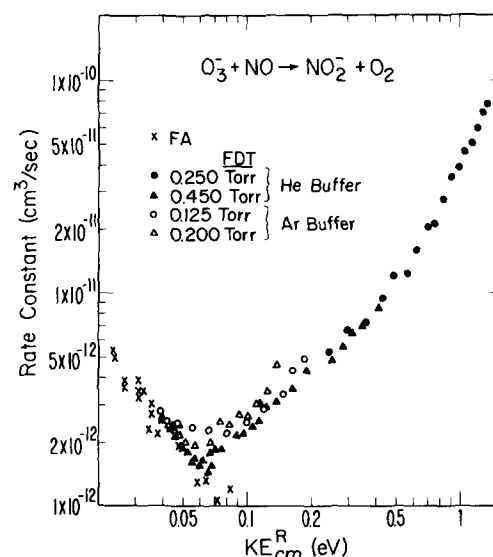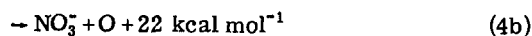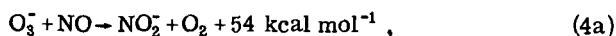


FIG. 2. Rate constants for the reaction $O_3^- + NO$ as a function of $KE^R_{c.m.}$. Flowing afterglow (FA) results are denoted by $X$'s and the flow-drift tube (FDT) results in a He and Ar buffer gas by the open and closed symbols.

the measurements is ±50% for the FA results and ±30% for the FDT results.

## A. $O_3^- + NO$

The reaction

$$O_3^- + NO \rightarrow NO_2^- + O_2 + 54 \text{ kcal mol}^{-1} , \qquad (4a)$$

$$\rightarrow NO_3^- + O + 22 \text{ kcal mol}^{-1} \qquad (4b)$$

has two exothermic channels. The exothermicity values follow from electron affinity (EA) values of 49[20] and 55 kcal mol⁻¹ [21] for $O_3^-$ and $NO_2^-$, respectively, from the value of $\Delta H_{298}^\circ(NO_3^-)$ of −75 kcal mol⁻¹,[22] and from standard values of the heats of formation.[23] Channel (4a) was identified as the dominant channel in the present study. The present measurements yield $k_4 = 2.2(-12)$ and $2.6(-12)$ cm³ s⁻¹ at thermal energy in the FA and FDT system, respectively, which agree well within the measurement uncertainty. Our earlier FA measurement[24] at thermal energy gave a much higher value $1(-11)$ cm³ s⁻¹, and identified (4b) as the dominant channel. We surmise that an excessive amount of $O_3$ in the buffer gas used as the source gas to produce the $O_3^-$ ions could have invalidated the earlier result by reacting with both the reactant neutral NO and the primary product ion $NO_2^-$. The reaction of $O_3$ with NO produces $NO_2$ that reacts with $O_3^-$ at a faster rate than NO[21] and thereby could enhance the apparent rate constant of $O_3^-$ with NO. A small conversion of NO to $NO_2$ of ~3% would be required to account for the observed differences. In addition, since $NO_3^-$ is the product ion of the $O_3^- + NO_2$ reaction and since $O_3$ reacts with $NO_2^-$ to form $NO_3^-$,[21] channel (4b) would be identified as the dominant reaction channel.

From geometrical considerations, the $NO_2^-$ product found in the present investigation is more reasonable than the earlier reported $NO_3^-$ product, which, however, is also exothermic. Production of $NO_2^-$ involves a simple O⁻ transfer from $O_3^-$ to NO. Production of $NO_3^-$ would involve a considerable amount of molecular rearrangement, the breaking of both O–O bonds in $O_3^-$ and the formation of two new N–O bonds, an unlikely process.

In Fig. 2, the three data sets, agree within experimental error. We consider the higher temperature FA subject to higher uncertainty and feel, therefore, that these data are not necessarily in disagreement with the more precise FDT measurements. The agreement between the FDT data sets for He and Ar up to 0.2 eV is significant. From the results in Fig. 1 for $O_3^- + NO$, at a $KE_{c.m.}^R$ value of 0.2 eV, the value of $KE_{c.m.}^B$ is 0.07 eV for He and 0.22 eV for Ar. Thus, the $O_3^-$ internal modes will be characterized by the temperatures corresponding to these values 538 and 1692 K for steady-state conditions. The agreement between the He and Ar data sets indicates that reaction (4) is not sensitive to the vibrational and rotational energy of the reactants in this energy range.

## B. $O_3^- + SO_2$

The reaction

$$O_3^- + SO_2 \rightarrow SO_3^- + O_2 + [9.4 + EA(SO_3)] \text{ kcal mol}^{-1} \qquad (5)$$
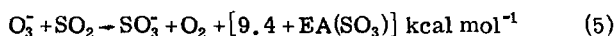
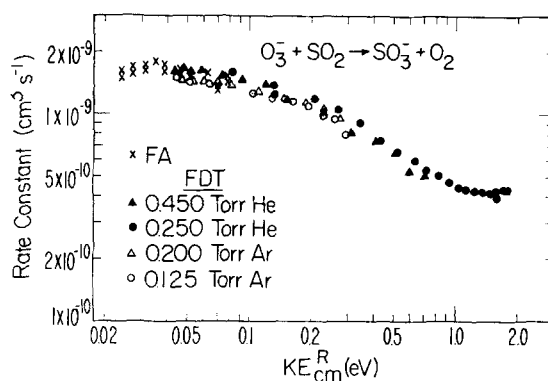is exothermic with the exothermicity uncertain by

FIG. 3. Rate constants for the reaction $O_3^- + SO_2$ as a function of $KE_{c.m.}^R$. Flowing afterglow (FA) results are denoted by $X$'s and the flow-drift tube (FDT) results in a He and Ar buffer gas by the open and closed symbols.

$EA(SO_3)$.[20,23] A lower limit of 1.7 eV has been found for $EA(SO_3)$.[25] The rate constant was measured to be $1.7(-9)$ cm³ s⁻¹ in both systems at thermal energy. Our earlier measurement[26] of $5.1(-10)$ cm³ s⁻¹ is felt to be in error. The present value is equal to the collision rate constant listed in Table I. The large dipole moment of $SO_2$, 1.6 D, results in $k_c = 2.1 k_L$ where $k_L$ is the Langevin collision rate constant determined from the neutral polarizability. As in the case of reaction (4), the FDT data for reaction (5) for He and Ar buffer gases represent very different ion internal temperatures. Thus, the agreement between the various data sets in Fig. 3 indicates that reaction (5) is also not sensitive to the internal energy of the reactants.

## C. $CO_3^- + NO$

The reaction

$$CO_3^- + NO \rightarrow NO_2^- + CO_2 + 41 \text{ kcal mol}^{-1} \qquad (6)$$
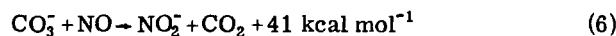
is exothermic, following from $\Delta H_f(CO_3^-) = -122$ kcal mol⁻¹[10] and Refs. 21 and 23. The rate constant was measured to be $1.0(-11)$ and $1.1(-11)$ cm³ s⁻¹ at thermal energy in the FA and FDT systems, respectively. These values are in good agreement with an earlier measurement of $9(-12)$ cm³ s⁻¹.[24] This earlier measurement was made without an excess of $O_3$ which interfered in the earlier measurement of reaction (4). As above, the agreement between the various data sets in Fig. 4 indicates that reaction (6) is not sensitive to the internal energy of the reactants.
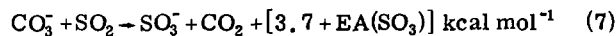
## D. $CO_3^- + SO_2$

The reaction

$$CO_3^- + SO_2 \rightarrow SO_3^- + CO_2 + [3.7 + EA(SO_3)] \text{ kcal mol}^{-1} \qquad (7)$$

is exothermic with exothermicity uncertain by $EA(SO_3)$.[10,23,25] The rate constant was measured to be $3.5(-10)$ and $4.0(-10)$ cm³ s⁻¹ at thermal energy in the FA and FDT systems, respectively. No previous thermal energy measurements have been made of this rate constant. The agreement between the FDT data sets in the He and Ar buffer indicate that reaction (7) is not sensitive to the ion internal energy. There is,
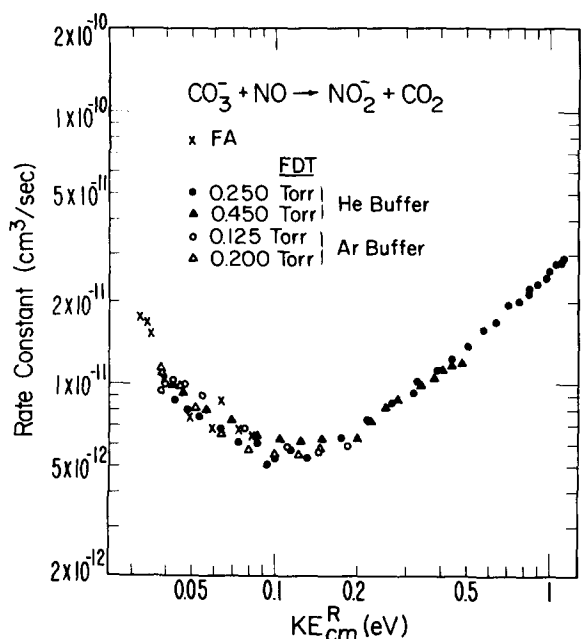
FIG. 4. Rate constants for the reaction $CO_3^- + NO$ as a function of $KE_{c.m.}^R$. Flowing afterglow (FA) results are denoted by $X$'s and the flow-drift tube (FDT) results in a He and Ar buffer gas by the open and closed symbols.

TABLE I. Thermal energy rate constants.

| Reaction | $k(cm^3 s^{-1})$ | | $k_c(cm^3 s^{-1})$[a] |
|---|---|---|---|
| | FA | FDT | |
| 4. $O_3^- + NO \rightarrow NO_2^- + O_2$[b] | 2.2(−12) | 2.6(−12) | 8.5(−10) |
| $\rightarrow NO_3^- + O$ | | | |
| 5. $O_3^- + SO_2 \rightarrow SO_3^- + O_2$ | 1.7(−9) | 1.7(−9) | 1.8(−9) |
| 6. $CO_3^- + NO \rightarrow NO_2^- + CO_2$ | 1.0(−11) | 1.1(−11) | 8.2(−10) |
| 7. $CO_3^- + SO_2 \rightarrow SO_3^- + CO_2$ | 3.5(−10) | 4.0(−10) | 1.7(−9) |

[a]From variational calculations in Ref. 19.
[b]Observed to be the predominant product channel.

however, some systematic difference between the FA and FDT data sets. Such a difference could indicate the effect of internal excitation of the neutral reactant $SO_2$ on the reaction rate constant. Due to the small difference within the measurement uncertainties, no definitive conclusions can be drawn.

### E. $O_3^- + CO_2$

The reaction

$$O_3^- + CO_2 \rightarrow CO_3^- + O_2 + 13 \text{ kcal mol}^{-1} \quad (8)$$

is an exothermic O⁻-transfer reaction similar to those in the present study. This reaction has been studied previously in our laboratory in both the FA and FDT systems[10] and by Lifshitz *et al.*[11] In the former, the reaction rate constant was found to be near the Langevin value at thermal energy and reduced by a factor of 4 at 0.2 eV. The good agreement that exists among the FA and FDT data sets suggests that reaction (8) is also insensitive to the internal energy of the reactants. In the latter, the measurements were made above 0.3 eV kinetic energy for $O_3^-$ ions partially in an excited state and, hence, could not address the internal energy dependence of the reaction.

### F. Dependence on $KE_{c.m.}^R$

For reactions (4) and (6), the dependence of the rate constant on $KE_{c.m.}^R$ shows a similar behavior, i.e., an initial decrease of $k$ with increasing $KE_{c.m.}^R$ followed by an increase. We have observed this behavior in most of the slow reactions of positive ions that have been studied in our laboratory. Slow in this context means that the reaction rate constant is small compared to the collision rate constant. The initial decrease of $k$ with

increasing $KE_{c.m.}^R$ has been interpreted[6,15,27] as indicating that the reaction goes through an intermediate complex. The lifetime of the complex decreases with increasing energy content, a feature of any unimolecular decomposition theory, and the small probability $(k \ll k_c)$ of the complex exiting by way of the most exothermic product channel decreases with decreasing complex lifetime.[27]

In the present study, reactions (5) and (7) have the largest rate constants. Reaction (5) has a moderate decrease in rate constant with energy while reaction (7) has a correspondingly large decrease. For positive ion−molecule reactions having rate constants equal to the collision rate constant at thermal energy, it is uncommon to observe a large decrease in the rate constant with increasing $KE_{c.m.}^R$ below several eV. However, it is reasonable that ion−atom interchange processes decrease in efficiency at some elevated energy.

### G. Dependence on ion internal energy

A measure of the effect of ion internal energy on reaction rate constants is provided by measurements in the FDT system in different buffer gases. The ion internal energy is characterized by $KE_{c.m.}^B$ at a particular value of $KE_{c.m.}^R$ as shown in Fig. 1.[1] This characterization
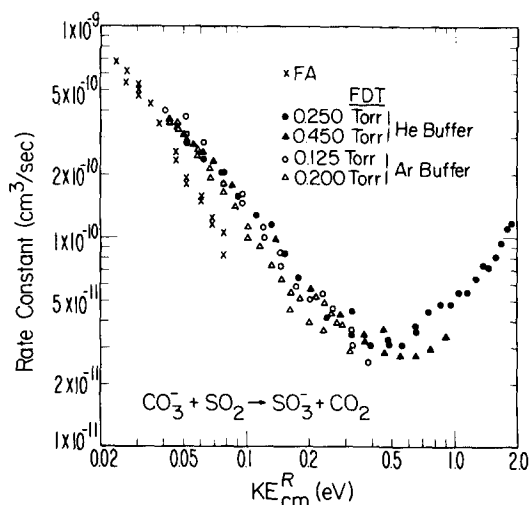


FIG. 5. Rate constants for the reaction $CO_3^- + SO_2$ as a function of $KE_{c.m.}^R$. Flowing afterglow (FA) results are denoted by $X$'s and the flow-drift tube (FDT) results in a He and Ar buffer gas by the open and closed symbols.

assumes that the ion-buffer gas collisions reach steady state in the FDT system. The data in Figs. 2–5 show no indication of an effect of vibrational excitation on the rate constant. Large vibrational effects have been observed for positive ion reactions[1–3] but there is no general theory that requires or predicts such effects. Qualitatively, one might expect an O⁻ transfer reaction to be facilitated by vibrational excitation in the $O_2$–O⁻ bond that is to be broken, but this apparently does not occur.

The steady state assumption implies that, on the average, a drifting ion has sufficient collisions with the buffer gas atoms to reach equilibrium among all degrees of freedom in the ion-buffer collision complex. Also implied is that the time to reach steady state is less than the average time between collisions of the ion with the reactant neutral. Thus, steady state conditions, as given by Fig. 1 for the $O_3^-$ reactions, represent an upper limit to the level of internal excitation of the reactant ions.

In the FDT, the distribution of *translational* energy states will reach steady state at some value of $E/N$ in a time much shorter than the drift time for the present conditions.[28] The distribution of *rotational* states is expected to behave similarly. Preliminary measurements of the distribution of rotational states in $N_2^+$ drifting in He have shown the steady state assumption to be valid.[29] No *direct* measurements of the *vibrational* state distribution of drifting ions have been made for either positive or negative ions. In addition, no enhancement of the reaction rate constant for vibrationally excited negative ions has been observed, although few systems have been studied.

The observation of large enhancements of reaction rate constants for $O_2^+$[1,2], $N_2OH^+$, $COH^+$, and $CO_2^+$[1,3] ions in an Ar buffer has been interpreted to be a result of ion internal excitation, although steady state conditions cannot be assumed to apply. The results for quenching of vibrational excitation of ions drifting in He suggests that positive ions are not vibrationally excited in He.[1] Thus, the steady state assumption may not be valid in this case and serves only as an upper limit. In the present study, the lack of steady state in a He buffer would only serve to enhance any effect of vibrational energy as measured by the difference between the rate constant in a He and Ar buffer gas.

The collisional dissociation of both $O_3^-$ and $CO_3^-$ ions have been observed in FDT experiments.[10,30] The observation of dissociation suggests that these ions are vibrationally excited in Ar since dissociation is usually viewed as a vibrational ladder-climbing process. These experiments are difficult to interpret quantitatively and thus cannot be used at present to check for steady state conditions.

In the FA, the distribution of translational and rotational states will reach steady state in a time much shorter than the ion residence time as in the FDT. Since He has been noted to be inefficient at vibrationally exciting ions under certain conditions in the FDT, the distribution of vibrational states in the FA may also not

reach steady state. However, the presence of the reactant ion precursor gases in the He buffer gas will help promote vibrational equilibration over that in pure He. In this study, $O_3$ and $CO_2$ precursor gases comprised up to 10% of the buffer gas flow in the FA and were added in such a way as to insure equilibrium with the apparatus wall temperature. In the FDT, this level is maintained <1% in order not to alter the transport properties of the ions from those in a pure buffer gas. Ion collisions with $O_3$ and $CO_2$ in the FA are expected to be more efficient than He in reaching vibrational steady state. In addition, the level of vibrational excitation at steady state at the maximum temperature in the FA is much less than that at the maximum value of $E/N$ in the FDT. Thus, the vibrational distribution can never be far from steady state in the FA. At the maximum FA temperature of 900 K, the majority of ions still occupy the ground vibrational state in steady state for a level spacing of 0.1 eV.

## IV. CONCLUSIONS

The rate constants for the O⁻ transfer reactions of $O_3^-$ and $CO_3^-$ with NO and $SO_2$ were found to have a significant dependence on the reactant center-of-mass kinetic energy near thermal energy. The reactions have little or no vibrational or rotational energy dependences as inferred from their similar reaction rates in He and Ar buffer gases in the FDT system. In the reactions that are slow at thermal energy, complex formation is presumed because of the negative kinetic energy dependence of the rate constant.

The lack of vibrational enhancement of these negative ion–molecule reactions is in sharp contrast to the enhancement widely observed in positive ion–molecule reactions. It remains to be determined if this lack of enhancement is a general feature of negative ion–molecule reactions. If so, this difference between negative and positive ion reactions will have important implications for all areas of ion chemistry research. Underlying the conclusions in this study is the assumption of steady state conditions. It is hoped that future experiments will provide evidence of the level of internal excitation in negative ions in drift tubes in order that this assumption be tested.

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