Rate constants for quenching the $^2A_2$ state of SO$_2^+$ by atmospheric gases

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The effect of ion source pressure on the cross sections for photodissociation of SO$_2^+$ has been measured systematically at $A_{\text{int}}$ = 4735 and 4795 Å. Using a Stern-Volmer treatment modified to account for the dependence of source residence time on pressure, rate constants have been measured for quenching the $^2A_2$ ($v_1v_3 = 3,3$) and $^2A_2$ ($v_1v_3 = 3,0$) states of SO$_2^+$ by N$_2$, SO$_2$, CO$_2$, and N$_2$. With SO$_2$ and N$_2$ as quenchers the rate constants range between 1.0 and 6.5 times the theoretical thermal capture rate constants ("Langevin limit"). The occurrence of several resonant and many near-resonant charge transfer processes is proposed to explain the unusually large rate constants.

I. INTRODUCTION

In the course of obtaining the ion photodissociation spectrum of SO$_2^+$, which we have recently reported in this Journal,$^7$ we have observed that the measured cross sections for photodissociation in the visible region were dependent upon the pressure of SO$_2$ used in the ion source. Since our previous work using the same ion source had shown no pressure effect on the photodissociation cross sections of N$^+$,$^8$ this observation was unexpected. At source pressures in the 0.01 to 0.10 Torr range ($\sim 30 \times$ the pressure used in gathering our previous SO$_2^+$ data) a significant effect on the photodissociation spectrum of Ar/$^2$S$_2^+$ had previously been observed in the same ion source, however.$^9$ This effect was interpreted in terms of collisional deactivation of vibrationally excited Ar/$^2$S$_2^+$ with a rate constant of 12% of Langevin. Thus, the pressure effect seen for SO$_2^+$ indicated some deactivation process occurring at a rate exceeding the theoretical upper limit for ion-molecular reactions. It therefore seemed important to make a systematic study of the processes involved and their precise rate constants.

II. EXPERIMENTAL METHOD

The ion photodissociation apparatus—a triple quadrupole system with coaxial irradiation of the ion beam by a flashlamp pumped dye laser—has been described in detail previously.$^1$ The first quadrupole transmitted only ions of a selected mass into the second quadrupole ("reactor quadrupole") with rf field only, where the only observable interaction with the laser beam occurred. The second quadrupole was adjusted to transmit either photoproduct ions or unreacted parent ions to the detector. Before beginning a systematic study of the pressure dependence of the photodissociation cross sections an MKS Baratron gauge equipped with a 1 Torr head was connected to one side of the ionization chamber via 1/4 in. o.d. (3/16 in. i.d.) tubing. Since sample gases flowed into the ionization chamber through a separate 1/4 in. o.d. tube connected at the opposite side of the chamber and the major escape path was through the 1/8 in. i.d. ion exit aperture (see the top half of Fig. 1), it was thought that the pressure measured in the Baratron head corresponded closely to that existing in the ionization region. There was no repeller in the ionization chamber.

Ions were produced by the impact of electrons accelerated through 50 V from a hot rhenium filament to the ionization chamber which they entered through a 1 mm hole. When the pressure in the ionization chamber was changed, the current through the filament was manually adjusted (in the opposite direction) to keep a constant ion beam current in the reactor quadrupole. Typically, the total emission from the filament was changed from 40 to 1 Torr as the pressure in the ionization chamber was raised from 0.5 to 8.0 m Torr. This adjustment was intended to avoid changes in the ion beam profile and possible saturation effects on the ion-counting system which could have produced artificial pressure effects. No significant effect of changing only the filament emission on the photodissociation cross sections was observed.

In order to obtain quenching rate constants from the pressure dependence of the photodissociation cross sections it was necessary to determine the average residence time of the SO$_2^+$ ions in the ion source. For this purpose, about half-way through this study, a grid (82% transmitting Ni mesh) was installed between the filament and the ionization chamber, as shown in the top half of Fig. 1. This grid was normally biased slightly negative with respect to the filament until the arrival of a positive voltage pulse 0.4-0.5 μs wide from an EH 132 A-8 pulse generator, which caused a burst of electrons to enter the ionization chamber. A second pulse generator (Hewlett Packard 214 A), triggered by the first with a adjustable time delay, delivered a +95 V pulse, 0.4-0.5 μs wide, to the ion accelerating plate located next to the ion exit hole in the ionization chamber. The timing sequence for the pulses is shown in the lower half of Fig. 1. This second pulse produced a dip in the peak of ion counts seen on the time-of-flight spectrum of the ions produced by the initial burst of electrons, as shown in Fig. 2. The time delay (measured on a Tektronix 5111 oscilloscope) between the two voltage pulses which centered the dip in the top of the TOF peak was taken to equal the average residence time in the ionization chamber $\left(\frac{1}{2}t_{\text{int}}\right)$ plus the flight time of the ions between the ion exit hole and the accelerating plate $\left(\frac{1}{2}t_{\text{acc}}\right)$:

$$Y_m = Y_i + Y_f \quad (1)$$
and CO

FIG. 2 Time-of-flight spectrum of \( \text{SO}_2^+ \) formed by pulsing electron beam on. \( \Delta t \) = time between pulsing electron beam on \( E_v = +4 \text{ V} \) and applying +95 V pulse to ion accelerating plate \( F_v \). \( P = 0.7 \text{ mTorr} \) (89% CO + 11% \( \text{SO}_2 \)). \( E_1, E_2, E_3 \) = ion kinetic energies in the source, reactor, and analyzer quadrupoles, respectively.

The flight time \( \tau \) was calculated from

\[
\tau = \left( \frac{2dm}{eE} \right)^{1/2},
\]

where \( d \) = the distance from the ion exit hole to the center of the accelerating plate = \( 2.86 \times 10^{-2} \text{ m} \), \( E \) = the voltage gradient over that distance = \( 3.50 \times 10^4 \text{ V m}^{-1} \), and \( m \) = the mass of the \( \text{SO}_2^+ \) ions. The calculated value was \( \tau = 0.33 \mu \text{s} \).

The values of \( \tau_m \) were found to increase linearly with the pressure in the ionization chamber. The best fit of the pressure dependence of the source residence times was given by

\[
\tau_s = 2.6( \pm 0.2) + 0.17( \pm 0.02)P,
\]

where \( \tau_s \) is in \( \mu \text{s} \) and the pressure is in mTorr. The indicated error ranges are standard deviations from a least-squares fit to residence times determined at seven pressures ranging from 0.5 to 7.1 mTorr. Other equations tried, which were less accurate in fitting the observed pressure dependence, included: \( \ln \tau_s \) vs \( P \), \( \tau_s^{-1} \) vs \( P^{-1} \), and \( \tau_s^{-1} \) vs \( P^{-1/2} \). The latter two functions, predicted to describe the mobility of ions for low, and for moderately strong, ratios of electric field to gas density \( (E/N) \), respectively, predict a stronger pressure dependence than actually observed. For the sake of comparison, the residence time of neutral molecules in the ion source was 1.2 ms when \( P = 3.2 \text{ mTorr} \).

Photodissociation cross sections measured after modifying the ion source for the double-pulse measurements of residence times showed a significantly smaller dependence on pressure than those measured before the modifications. This difference may be due to the effect of the control grid (biased 33 V positive with respect to the filament in the quenching experiments performed after the measurement of the source residence times) on the electric field inside the source. The two sets of quenching data were made consistent by multiplying the values of \( \tau \), calculated from Eq. (3) by the factor 2.05 before plotting the data from the earlier experiments in Figs. 4 and 5.

Gas mixtures were prepared on a stainless steel vacuum line equipped with three 1/ storage bulbs and four Bourdon tube pressure gages (0-1000 Torr range, smallest scale division = 10 Torr). In the case of \( \text{SO}_2 + \text{N}_2 \text{O} \) and \( \text{SO}_2 + \text{CO} \), mixtures a measured amount of each gas was frozen from different storage bulbs into a single glass nipple, then flash-vaporized into a third storage bulb which had previously been evacuated. In the case of \( \text{SO}_2 + \text{N}_2 \) known amounts of each gas were mixed by sudden expansion from their storage bulbs into the vacuum line, followed by a second rapid expansion into a third (evacuated) storage bulb. In this case the mixing was allowed to continue overnight. The compositions of the prepared mixtures, based on measured initial pressures, were: 80% \( \text{N}_2 \text{O} \) + 20% \( \text{SO}_2 \); 89% \( \text{CO} + 11\% \text{ SO}_2 \); and 89% \( \text{N}_2 + 11\% \text{ SO}_2 \). Mass spectral analyses run before and after using the mixtures confirmed these compositions within <2% except for the case of \( \text{N}_2 \text{O} + \text{SO}_2 \), which appeared to change from 80% to 87% \( \text{N}_2 \text{O} \) during the two day period in which that mixture was used. The gases used to make the mixtures were all of stated purities >99%; the \( \text{SO}_2 \), \( \text{N}_2 \text{O} \), and \( \text{CO} \) were subjected to at least one freeze (in liquid N) pump–thaw cycle to remove noncondensible impurities before use.

To confirm that the pressure in the ionization region was being measured accurately, and to obtain an estimate of the electric field present in the ionization region, a series of
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19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The effect of ion source pressure on the cross sections for photodissociation of $SO_2^+$ has been measured systematically at $\lambda = 4735$ and 4795 Å. Using a Stern-Volmer treatment modified to account for the dependence of source residence time on pressure, rate constants have been measured for quenching the $A^2A_2 (\nu_1=3,3)$ and $A^2A_2 (\nu_1=0,0)$ states of $SO_2^+$ by $N_2$, $SO_2$, $CO_2$, and $N_2$. With $SO_2$ and $N_2$ as quenchers the rate constants range between 1.0 and 6.5 times the theoretical thermal capture rate constants ("Langevin limit"). The occurrence of several resonant and many near-resonant charge transfer processes is proposed to explain the unusually large rate constants.
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measurements was made of the extent of the reaction

$$\text{CH}_4^+ + \text{CH}_4 \rightarrow \text{CH}_3^+ + \text{CH}_3$$

which occurred when pure (Research Grade) CH$_4$ was introduced into the ion source. These experiments were carried out immediately following the quenching experiments using the same operating conditions for the triple quadrupole mass spectrometer with the following exceptions: the ion energy in the second quadrupole (E$_2$) was changed from 3.9 to 16 eV; the rf voltage on the second quadrupole was reduced from 400 to 210 VAC; and both reactant (CH$_4^+$) ion currents were measured on a Faraday cup located at the end of the third quadrupole using a Cary 31 electrometer.

The observed dependence of the ratio of product ion current to reactant ion current upon the concentration of CH$_4$ in the ion source is shown in Fig. 3. The cross section for reaction (4) was calculated from Eq. (5),

$$\frac{I_{\text{CH}_3^+}}{I_{\text{CH}_4^+}} = \sigma I [\text{CH}_4],$$

where $I$ = the distance from the electron beam in the center of the ionization region to the ion exit hole = 0.38 cm. The result was $\sigma = 25.5 \text{ Å}$$. Comparison of this value with the literature data on the dependence of the cross section on average kinetic energy of the reactant ions$^5$ leads to the following value for the electric field strength present in our ion source: $E = 8.1 \text{ V/cm}$.

The preceding result was used to calculate a theoretical ion source residence time, using an equation by Field, Franklin, and Lampe$^7$ (although in our case the electric field was due to penetration of fields from the ion accelerating plate and filament grid instead of established by a repeller plate), yielding $\tau_s = 2.5 \mu$s. This time agrees with our measured source residence time at the $P = 0$ limit, within our indicated experimental error.

III. RESULTS

Figures 4 and 5 show the effect of pressure in the ionization region upon the reciprocal of the measured photodissociation cross section for several gas mixtures and two irradiation wavelengths. The method of plotting the data is a modification of the classical Stern–Volmer treatment, taking into account the variation in source residence time reported in Sec. II. Equations for analyzing these data were

$$
\begin{align*}
\left( \frac{\tau_s \cdot P}{1 + k_f \cdot \frac{\lambda}{\lambda_0}} \right) \left( \mu \text{sec} \cdot \text{mTorr} \right) &= 0.02 \text{ cm}^2 \text{ molecule}^{-1} \\
\lambda_{irr} &= 4735 \text{ Å} \\
\lambda_{irr} &= 4795 \text{ Å} \\
\lambda_{irr} &= 4795 \text{ Å}
\end{align*}
$$

FIG. 4. Dependence of cross sections for SO$_2^\cdot + h\nu \rightarrow \text{SO}^+ + \text{O}$ on source pressure ($P$) and residence time ($\tau_s$). $\sigma_{\text{SO}^+}^0$ = limit of cross section when $P \rightarrow 0$. $k_f = 4.0 \times 10^7$ s$^{-1}$. For pure SO$_2$. 

FIG. 5. Dependence of cross sections for SO$_2^\cdot + h\nu \rightarrow \text{SO}^+ + \text{O}$ on source pressure and residence time for mixed gases.
derived from the following scheme of fundamental processes occurring in the ion source:

\[
\begin{align*}
\text{Process} & \quad \text{Rate} \\
\text{SO}_2 + e^- & \rightarrow \text{SO}_2^+ + 2e^- & \alpha_{i,\text{ion}}[\text{SO}_2] \quad (6) \\
\text{SO}_2 + e^- & \rightarrow \text{SO}_2^+ + 2e^- & \alpha_{f,\text{ion}}[\text{SO}_2] \quad (7) \\
Q + e^- & \rightarrow Q^+ + 2e^- & \alpha_{Q,\text{ion}}[Q] \quad (8) \\
\text{SO}_2^+ + \text{SO}_2 & \rightarrow \text{SO}_2^+ + \text{SO}_2^+ & \kappa_{\text{SO}_2}(\text{SO}_2^+) \cdot [\text{SO}_2] \quad (9) \\
\text{SO}_2^+ + Q & \rightarrow \text{SO}_2^+ + Q^* & k_{\text{Q}}([\text{SO}_2^+])(Q) \quad (10) \\
\text{SO}_2^+ + Q & \rightarrow \text{SO}_2^+ + Q^* & k_{\text{SO}_2}(\text{SO}_2^+)(Q) \quad (11) \\
\text{SO}_2^+ + \text{SO}_2 & \rightarrow \text{SO}_2^+ + \text{SO}_2^+ & k_{\text{SO}_2}(\text{SO}_2^+) \quad (12) \\
Q^* + \text{SO}_2 & \rightarrow Q^* + \text{SO}_2^+ & k_{\text{R}}(Q^*)([\text{SO}_2] \quad (13) \\
\text{SO}_2^+ & \rightarrow (\text{SO}_2^+)_{\text{ion beam}} & k_e[\text{SO}_2^+] \quad (14) \\
\text{SO}_2^+ & \rightarrow (\text{SO}_2^+)_{\text{ion beam}} & k_i[\text{SO}_2^+] \quad (15)
\end{align*}
\]

The first three processes shown are ionization by electron impact. The \( ^* \) designation an observable electronically excited state. The next three processes represent energy transfer processes, electronic (including charge transfer) and vibrational, which deplete the population of a particular energy level in \( \text{SO}_2^+ \) from which a transition originates for a given \( Q \). The designates an observable electronically excited state-in the case of the 44\((X)-5200 \) A portion of the photodissociation spectrum of \( \text{SO}_2 \). Here \( \text{SO}_2 \), as well as those measured in this work, were calculated using the total beam current in the laser-ion interaction region. For \( \lambda_m \), 4187 A, however, only ions in the \( \tilde{A} \) state (or higher) of \( \text{SO}_2^+ \) are capable of photodissociation. Thus, the observed cross sections are related to the true cross sections for processes originating in the \( \tilde{A} \) state by

\[
\sigma_{\tilde{A}} = \frac{[\text{SO}_2^+] \exp(-k_e)}{[\text{SO}_2^+] + [\text{SO}_2^+]} \cdot \sigma_{\text{true}}. \quad (20)
\]

Equation (20) assumes the same relative population of the metastable ions in the ion beam as in the ion source except for a correction factor for radiative decay.* Substituting Eqs. (16)–(18) into Eq. (20) gives

\[
\sigma_{\tilde{A}} = \frac{k_u \alpha_{i,\text{ion}} \exp(-k_e)}{k_u + k_i}\left(\alpha_i + \alpha_e + (\alpha_e Q/(\text{SO}_2^+))\right). \quad (21)
\]

In the limit of zero pressure (for fixed composition) \( \beta = 0 \), and

\[
\sigma_{\tilde{A}} = \frac{k_e \alpha_{i,\text{ion}} \exp(-k_e)}{k_u + k_i}\left(\alpha_i + \alpha_e + (\alpha_e Q/(\text{SO}_2^+))\right). \quad (22)
\]

Dividing Eq. (22) by Eq. (21) yields

\[
\frac{\sigma_{\tilde{A}}}{\sigma_{\text{true}}} = 1 + \frac{\beta}{k_u + k_i} \quad (23)
\]

Using Eq. (20) and \( k_u = \gamma_c^{-1} \), where \( \gamma_c \) is given by Eq. (21), converts Eq. (20) into the equation used to fit the pressure dependence of the photodissociation cross sections:

\[
\frac{\sigma_{\tilde{A}}}{\sigma_{\text{true}}} = 1 + \frac{X_{\text{SO}_2} k_{\text{SO}_2} + X_{\gamma} (k_e + k_i)}{RT} \quad (24)
\]

The experimental data obtained in the study are plotted in Figs. 4 (\( X_{\text{SO}_2} = 0 \)) and 5 (\( X_{\text{SO}_2} = 0 \)), using the previously determined value of \( k_e = 4.0 \times 10^4 \text{ s}^{-1} \). The variables plotted are the same as in the classical Stern–Volmer treatment of fluorescence quenching, except that the pressure in the ion source is modified by a factor which accounts for the non-constant residence time: \( \gamma_c^{-1} = 1 + k_i \gamma_c \). Without this factor \( \sigma_{\tilde{A}}/\sigma \) vs \( P \) plots showed considerable curvature for pure \( \text{SO}_2 \) and for the \( \text{SO}_2 + \text{N}_2 \) mixture. Ten points obtained using the \( \text{SO}_2 + \text{N}_2 \) mixture (five at each wavelength) were omitted from Fig. 5 for the sake of clarity. Values of \( k_{\text{SO}_2} \) were obtained from the slopes of the least-squares lines shown in Fig. 4, using \( f = 323 \text{ K} \) in Eq. (24). These values of \( k_{\text{SO}_2} \) were then combined with the slopes of the lines shown in Fig. 5, and with the unplot data for \( \text{SO}_2 + \text{N}_2 \), to obtain values for \( k_e + k_i \), for \( Q = \text{N}_2, \text{O}_2, \text{CO}_2, \) and \( \text{N}_2 \). The resulting rate constants, in molecular units, are shown in Table I. The indicated uncertainties are obtained from the standard deviations of the slopes of the lines in Figs. 4 and 5.

The rate constants were converted into the quenching cross sections, shown in the last column of Table I, using the relation

\[
\alpha_{i,\gamma} = k_c / \tilde{r}. \quad (25)
\]

Here \( \tilde{r} \), the average velocity toward the exit hole of the ions in the ionization region, was estimated from \( \tilde{r} = \gamma_c^{-1} \), where \( i \) was defined in Sec. II and \( \gamma_c^{-1} \) is the source residence time at the limit of zero pressure. The resulting value for \( \text{SO}_2^+ \) is \( \tilde{r} = 1.4 \times 10^7 \text{ cm/s} \). A short series of measurements of the pressure depen-
dence of the photodissociation cross sections was made in the UV spectrum of SO$_2^+$, using pure SO, and $\lambda_{\text{ext}} = 3192$ Å. The cross sections were found to increase with increasing source pressure (in contrast to the data in the visible region) up to $P \sim 1$ mTorr, where a maximum was reached. Above 3 mTorr the cross sections began to decrease slowly with pressure; at higher pressures the value of $d(\sigma)/dT/d(P Y_1)$ approximated that found for the 89% N$_2$ + 11% SO$_2$ mixtures at $\lambda_{\text{ext}} = 4795$ Å. Since the major transition occurring at 3192 Å is thought to be $\tilde{X} \rightarrow \tilde{C}^2 B_1$, the low pressure results seem to confirm step (9), which augments the population of the $\tilde{X}$ state of SO$_2^+$, in the proposed quenching mechanism. The weaker pressure effect above 3 mTorr is consistent with a contribution at 3192 Å from an $\tilde{X} \rightarrow \tilde{C}$ transition originating from an excited vibrational level (we estimate that the $1_2^3 \Sigma^+$, $1_2^3 \Sigma^-$, and $1_2^3 \Pi^+$ bands, e.g., would lie near 3192 Å). Another possible contributor would be a second electronic transition, such as $\tilde{A} \rightarrow \tilde{B}$, (for which we predict an origin of $\lambda_{\text{ext}} = 3792$ Å).

**TABLE I. Quenching rate constants for SO$_2^+$ ($\tilde{A} \rightarrow \tilde{B}$)**

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$10^3 k_{SO}$ (cm$^3$ s$^{-1}$)</th>
<th>$10^3 (k_a + k_i)$ (cm$^3$ s$^{-1}$)</th>
<th>$\sigma_0$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>4735 Å</td>
<td>5.55 ± 0.06</td>
<td>106 ± 4</td>
</tr>
<tr>
<td>N$_2$O</td>
<td></td>
<td>2.52 ± 0.29</td>
<td>173 ± 20</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>0.22 ± 0.12</td>
<td>15 ± 22</td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td>-0.36 ± 0.20</td>
<td>-25 ± 14</td>
</tr>
<tr>
<td>$\lambda_{\text{ext}} = 4795$ Å</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO$_2$</td>
<td>3.63 ± 0.12</td>
<td></td>
<td>249 ± 38</td>
</tr>
<tr>
<td>N$_2$O</td>
<td></td>
<td>5.38 ± 0.45</td>
<td>368 ± 31</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>1.08 ± 0.20</td>
<td>27 ± 14</td>
</tr>
<tr>
<td>N$_2$</td>
<td></td>
<td>0.47 ± 0.20</td>
<td>32 ± 12</td>
</tr>
</tbody>
</table>

**TABLE II. Selected ionization potentials and vibrational frequencies**

<table>
<thead>
<tr>
<th>Specie</th>
<th>Electronic state</th>
<th>IP(eV)</th>
<th>$v_1$(cm$^{-1}$)</th>
<th>$v_2$(cm$^{-1}$)</th>
<th>$v_3$(cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_2$</td>
<td>$\tilde{X}^1 A_1$</td>
<td>0</td>
<td>1167</td>
<td>526</td>
<td>1381</td>
</tr>
<tr>
<td>SO$_2^+$</td>
<td>$\tilde{A}^2 A_1$</td>
<td>12.311*</td>
<td>(11511)</td>
<td>454</td>
<td>(1362)</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>$\tilde{A}^2 A_1$</td>
<td>13.030*</td>
<td>953</td>
<td>499</td>
<td>(1127)</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>$\tilde{X}^1 \Sigma^+$</td>
<td>0</td>
<td>1285</td>
<td>589</td>
<td>2224</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>$\tilde{X}^1 \Pi^1$</td>
<td>12.886</td>
<td>1126.2</td>
<td>456.8</td>
<td>1737.6</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>$\tilde{X}^1 \Pi^3$</td>
<td>12.902</td>
<td>1126.2</td>
<td>456.8</td>
<td>1737.6</td>
</tr>
<tr>
<td>CO</td>
<td>$\tilde{X}^1 \Sigma^+$</td>
<td>0</td>
<td>1333</td>
<td>667</td>
<td>2349</td>
</tr>
<tr>
<td>CO</td>
<td>$\tilde{X}^1 \Pi^1$</td>
<td>13.776</td>
<td>1266</td>
<td>508</td>
<td>1472</td>
</tr>
<tr>
<td>N$_2$</td>
<td>$\tilde{X}^1 \Sigma^+$</td>
<td>0</td>
<td>1319*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N$_2$</td>
<td>$\tilde{X}^1 \Pi^1$</td>
<td>15.580</td>
<td>2207*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*All vibrational frequencies are from Ref. 29, unless otherwise noted; corrections for anharmonicity were applied in the case of SO$_2^+$ and SO$_2^*$ (Å) only.

4 Calculated from the fourth IP = 15.992 ± 0.003 eV for SO$_2^+$ (Ref. 27) and the negatively assigned $\lambda_{\text{ext}} = 3368 ± 1$ Å for $\tilde{A} \rightarrow \tilde{B}$ in SO$_2^+$ (Ref. 1). Previously reported values for the first IP of SO$_2$ are 12.30 ± 0.01 (Ref. 12) and 12.348 ± 0.002 eV (Ref. 28).

6 From Ref. 1. $v_1$ and $v_3$ in the $\tilde{A}$ state were taken to be the same as for SO$_2$ (Ref. 26) and $v_2$ in the $\tilde{A}$ state was estimated assuming $v_1 = v_2 = v_3 = 1.183$.

7 Calculated from the fourth IP = 15.992 ± 0.003 eV for SO$_2^+$ (Ref. 27) and $\lambda_{\text{ext}} = 4187 ± 1$ Å for $\tilde{A} \rightarrow \tilde{B}$ in SO$_2^+$ (Ref. 1).

8 = 0.002 eV, from Ref. 29 Other reported values are 12.889 (Ref. 30) and 12.893 ± 0.005 eV (Ref. 31)

9 The $v_2$ and the $1_{1/2}^3 \Sigma^+$ splitting is from Ref. 25.

IV. DISCUSSION

The ratios of the experimentally determined quenching rate constants to theoretical rate constants are plotted vs the differences between the first ionization potentials of the quenchers and SO$_2$, in Fig. 6. The “theoretical” rate constants are thermal capture rate constants for collisions of SO$_2^+$ and the quencher, calculated using the parametrization of Su and Chesnavich, which was estimated by those authors to be accurate to < 3%. We used the following polarizabilities and dipole moments in the calculations: $\alpha = 4.28$ (SO$_2$), 3.03 (N$_2$O), 2.911 (CO$_2$), and 1.74 (N$_2$) Å$^3$; $\mu = 1.63$ (SO$_2$) and 0.16 (N$_2$O) D. The strong dependence of $k_0/k_{10}$ on the ionization potential of the quencher indicates that electronic energy transfer is the major pathway for quenching, at least for $Q = SO_2$ and N$_2$O. The “peak” observed in Fig. 6 matches well with the location of the $\tilde{A}$ state of SO$_2^+$, which lies 0.719 eV above the $\tilde{X}$ state (see Table II). This observation provides further confirmation that it is the $\tilde{A}$ state of SO$_2^+$ which is being quenched at $\lambda_{\text{ext}} = 4735$ and 4795 Å.

A brief review of selected literature on the quenching of excited states of ions by small neutral molecules shows the following trends:

(a) Quenching rate constants usually increase with increasing vibrational quantum number in the donor.

(b) Ions in electronically excited states react more rapidly than the corresponding ions in ground electronic states.

(c) An applied electric field (increasing ion velocity), has
only a small effect on the rate of some exothermic charge transfer reactions of $O_2^+$, but a stronger effect on charge transfer reactions of $CO_2^+$, $N_2O^+$, and $SO_2^+$. It is generally assumed, however, that the rate constant never exceeds $k_{TB}$. 

It has also commonly been accepted that a small $\Delta E$ and large Franck-Condon factors are necessary for the quenching process to be fast. In the present study the ions being quenched are highly vibrationally excited ($v_i = 3$ for both wavelengths used, plus $v_j = 3$ when $\lambda_{\text{max}} = 4795 \text{ Å}$) as well as electronically excited so that large quenching rate constants would be expected if $\Delta E$ is small and the Franck-Condon factors are favorable. Figure 6 also shows that all $k_q$'s increase when $v_i$ is increased from 0 ($\lambda_{\text{max}} = 4735 \text{ Å}$) to 3 ($\lambda_{\text{max}} = 4795 \text{ Å}$).

In the case where $Q = N_2O$ the following processes are calculated, using the data shown in Table II, to provide essentially resonant pathways for quenching by charge exchange:

$$SO_2^+ (\tilde{X}^1 A_2, 330) + N_2O \rightarrow SO_2 (340) + N_2O^+ (\tilde{X}^1 \Pi_{\gamma}, 000), \Delta E = 108 \text{ cm}^{-1}, (26)$$

$$SO_2^+ (\tilde{X}^1 A_2, 300) + N_2O \rightarrow SO_2 (310) + N_2O^+ (\tilde{X}^1 \Pi_{\gamma}, 000), \Delta E = -6 \text{ cm}^{-1}. (27)$$

Not only is $\Delta E$ nearly zero, within the combined uncertainty ($\pm 50 \text{ cm}^{-1}$) of the two ionization potentials used to calculate the quantity, but the Franck-Condon factors are large also because $\Delta v_i = 0$ and $\Delta v_j = 1$ to 8 for the strongest peaks in the first band of the photoelectron spectrum of $SO_2^+$.

In addition to reactions (26) and (27), 43 exothermic charge transfer processes are predicted to be possible from the $v_i v_j v_k$ = 330 vibrational level and 34 processes from the 300 level of the $\tilde{A}$ state of $SO_2^+$, to yield either the $\tilde{X}^1 \Pi_{\gamma}$, or $\tilde{X}^1 \Pi_{\gamma}$, states of $N_2O^+$, subject to the restriction that $v_i < 5$ and $v_j < 5$ in the neutral $SO_2$ product. Still more exothermic processes may be written yielding $N_2O^+$ with $v_i = 1$ or 2, which vibrational levels are split by the Renner effect into ten states lying within 0.139 eV (1122 cm$^{-1}$) of $\tilde{X}^1 \Pi_{\gamma}$, 000. One example of such a process is

$$SO_2^+ (\tilde{A}^2 A_2, 330) + N_2O \rightarrow SO_2 (330) + N_2O^+ (\tilde{X}^1 \Pi_{\gamma}, 1010), \Delta E = +27 \text{ cm}^{-1}, (28)$$

where the notation used for the spin-vibronic level of $N_2O^+$ is taken from Callomon and Creutzberg. The rate constants listed under the heading "$k_r + k_{nr}$" for $Q = N_2O$ in Table I are the sums of the rate constants for all processes which deexcite the previously indicated excited states. Based on the results obtained with $Q = CO_2$ and $N_2$ (see below), however, we conclude that $k_{nr} >> k_r$, when $Q = N_2O$ or $SO_2$.

In the case where $Q = SO_2$, step (9) in the reaction scheme proposed above includes two distinct processes. The first process is collision-induced internal conversion of $SO_2^+$ from the $\tilde{A}^2 A_2$ state to the $\tilde{X}^1 A_2$ state with the decrease in electronic energy of the ion equaling the increase in its vibrational energy. Examples of this process for the two vibronic states of $SO_2^+$ whose quenching rates were measured in our study are

$$SO_2^+ (\tilde{A}^2 A_2, 330) + SO_2 \rightarrow SO_2^+ (\tilde{X}^1 A_2, 590) + SO_2, \Delta E = -111 \text{ cm}^{-1}, (29)$$

$$SO_2^+ (\tilde{A}^2 A_2, 300) + SO_2 \rightarrow SO_2^+ (\tilde{X}^1 A_2, 560) + SO_2, \Delta E = -90 \text{ cm}^{-1}. (30)$$

Since $\Delta v_i = +2$ for the ion, the Franck-Condon factors may not be as large as for reactions (26) and (27). Also, the calculated $\Delta E$'s may not be very accurate since no anharmonicity constants were available to use for predicting vibrational energies in the $X$ state of $SO_2^+$.

The second quenching process when $Q = SO_2$ is charge transfer. Example reactions which are nearest to resonance (subject to the restrictions $\Delta v_i = \Delta v_j = 0$ in the donor and $v_i < 5, v_j < 10$ in the product ion) are

$$SO_2^+ (\tilde{A}^2 A_2, 330) + SO_2 \rightarrow SO_2^+ (\tilde{X}^1 A_2, 260), \Delta E = +21 \text{ cm}^{-1}. (31)$$

$$SO_2^+ (\tilde{A}^2 A_2, 300) + SO_2 \rightarrow SO_2^+ (\tilde{X}^1 A_2, 300) + SO_2, \Delta E = -80 \text{ cm}^{-1}. (32)$$

Subject to the same restrictions, another exothermic 31 and 32 state-to-state reactions may be written for $v_i v_j v_k$ = 330 and 300 levels of $SO_2^+$, respectively.

In the case where $Q = CO_2$, charge transfer from the $\tilde{A}$ state of $SO_2^+$ is endothermic by 6013 ± 50 cm$^{-1}$. Thus, $k_{q,C}$ would be expected. This expectation is supported by the fact that $k_{q,C} (4795 \text{ Å}) - 5 k_{q,N} (4735 \text{ Å})$ reflecting the greater ease of transferring a quantum from the low energy bending mode ($v_1$) via

$$SO_2^+ (\tilde{A}^2 A_2, 330) + CO_2 \rightarrow SO_2^+ (\tilde{A}^2 A_2, 320) + CO_2 (010), \Delta E = +251 \text{ cm}^{-1}. (33)$$

than from the higher energy symmetric stretching mode via

$$SO_2^+ (\tilde{A}^2 A_2, 300) + CO_2 \rightarrow SO_2^+ (\tilde{A}^2 A_2, 200) + CO_2 (010), \Delta E = +421 \text{ cm}^{-1}. (34)$$

It is also possible that quenching by $CO_2$ could occur via collision-induced internal conversion, analogous to reactions (29) and (30). It is not clear, however, why the rate constant for internal conversion should decrease by factors of 3.4 (at 4795 Å) and 7 (at 4735 Å) when the quencher is changed from $SO_2$ to $CO_2$. A simpler interpretation of all our data is that the faster quenching by $SO_2$ and $N_2O$ proceeds predominantly by charge transfer and that the results obtained for $CO_2$ measure the combined rate of $V-V$ energy transfer and collision-induced internal conversion.

The still smaller quenching rate constants obtained for $Q = N_2$, reflect the fact that the transfer of a single vibrational quantum would be endothermic by an amount much greater than 3/2 $RT (340 \text{ cm}^{-1})$:

$$SO_2^+ (\tilde{A}^2 A_2, 330) + N_2 \rightarrow SO_2^+ (\tilde{A}^2 A_2, 320) + N_2 (1), \Delta E = +1465 \text{ cm}^{-1}. (35)$$

The negative value of the rate constant for quenching the $v_i v_j v_k$ = 300 level of the $\tilde{A}$ state of $SO_2^+$ is probably real, resulting from the rate of populating it by collision from
levels with $v_2 > 0$ being faster than the rate of depopulating it by removing a quantum from $v_1 = 3$. This effect of collision on the cascading from higher to lower energy levels does, of course, complicate the interpretation of all our data, but we believe it to be of minor importance in the cases of the larger rate constants measured.

As mentioned above it is often assumed that the thermal capture rate constants calculated by equations such as Su and Chesnavich's provide an upper limit to experimentally determined rate constants for ion–molecule reactions. The results which we show in Table I and Fig. 6, however, exceed that upper limit by up to a factor of 6.5. It must be acknowledged that our $k_{q2}$'s are not strictly thermal rate constants, since our SO$_2$ ions acquire a kinetic energy of $\leq 3.08$ eV while being accelerated out of our ion source by the field penetrating from the ion accelerating plate. We feel, however, that the effect of kinetic energy is unlikely to be large enough to entirely account for the large $k_{q2}/k_{th}$ ratios we observed. Of greater significance is the combined effect of vibrational and electronic excitation and the existence of many resonant or near-resonant channels by which charge transfer can occur.

To put our results in perspective three of our rate constants are compared in Table III with seven other recently published values. In all cases except the first one specific vibronic states were monitored. Most measurements of the rate of ion–molecule reactions yield rate constants averaged over many vibrational states, and possibly even over several electronic states, thus obscuring any very fast resonant processes. The very strong enhancement of rate constants for processes having $\Delta E < RT$ ($\sim 210$ cm$^{-1}$ in our case) has been shown by Kato et al. who calculate that 50% of reaction (5) in Table III proceeds via the state specific process:

$$\text{NO}^+ + \text{CS} \rightarrow 2\text{Ar} + \text{CS}^+$$

with $28$ channels were energetically attainable at the collision energy used. The model used in the calculation of Kato et al. applies to charge transfer occurring via a simple electron jump mechanism at large interaction distances. This model would appear to be appropriate to describe the majority of the quenching of SO$_2$ by N,O and by SO, and, as shown above, a number of channels exist in these cases which have even smaller $\Delta E$'s than does Eq. (36).

Based on our results and the above considerations, we suggest that many more reactions having $k_{q2} > k_{th}$ can be discovered using recently developed techniques for studying state-to-state reactions between ions and molecules in which $\Delta E < RT$.

### ACKNOWLEDGMENTS

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#### Table III. Selected charge transfer rate constants exceeding $k_{th}$

<table>
<thead>
<tr>
<th>No.</th>
<th>Reaction</th>
<th>$T$ (K)</th>
<th>$KE_{cn}$ (eV)</th>
<th>$k_{q2}/k_{th}$</th>
<th>Method</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>Ar$^+$ + CS $\rightarrow$ 2Ar + CS$^+$</td>
<td>300</td>
<td>0.55</td>
<td>1.16 ± 0.06</td>
<td>SIFT-DRIFT</td>
<td>36</td>
</tr>
<tr>
<td>(2)</td>
<td>D$_2$ $\rightarrow$ (e) + N$_2$ + D$_2$ + N$_2$</td>
<td>$\sim$ 400</td>
<td>1.0</td>
<td>1.48 ± 0.37</td>
<td>PIRFG$^a$</td>
<td>37</td>
</tr>
<tr>
<td>(3)</td>
<td>H$_2$ $\rightarrow$ (e) + N$_2$ + H$_2$ + N$_2$</td>
<td>$\sim$ 400</td>
<td>1.0</td>
<td>1.60 ± 0.40</td>
<td>PIRFG$^a$</td>
<td>37</td>
</tr>
<tr>
<td>(4)</td>
<td>N$_2$' ($\beta$ $\Sigma^+_g$, $v_1 = 1$) + N$_2$ + N$_2$ + N$_2$</td>
<td>300</td>
<td>1.4</td>
<td>1.67 ± 0.28</td>
<td>PIRFG</td>
<td>37</td>
</tr>
<tr>
<td>(5)</td>
<td>NO$^+$ (a $\Delta^3\Pi$, $v = 2$) $\rightarrow$ Ar + NO + Ar$^+$</td>
<td>$\sim$ 400</td>
<td>1.0</td>
<td>2.17 ± 0.34</td>
<td>IPDS</td>
<td>This work</td>
</tr>
<tr>
<td>(6)</td>
<td>H$_2$ $\rightarrow$ (e) + CO + H$_2$ + CO$^+$</td>
<td>400</td>
<td>0.7$^a$, 0.28</td>
<td>2.2$^a$, 0.07</td>
<td>IPDS</td>
<td>This work</td>
</tr>
<tr>
<td>(7)</td>
<td>SO$_2$' (a $\Delta^3\Pi$, $v = 3$) + SO$_2$ + SO$_2$</td>
<td>323</td>
<td>0.6$^a$, 0.28</td>
<td>3.0$^a$, 0.35</td>
<td>IPDS</td>
<td>This work</td>
</tr>
<tr>
<td>(8)</td>
<td>CO$^+$ (a $\Delta^3\Pi$, $v = 30$) + N$_2$ + SO$_2$ + N$_2$</td>
<td>323</td>
<td>0.6$^a$, 0.28</td>
<td>3.0$^a$, 0.35</td>
<td>IPDS</td>
<td>This work</td>
</tr>
<tr>
<td>(9)</td>
<td>D$_2$ $\rightarrow$ (e) + CO + H$_2$ + CO$^+$</td>
<td>$\sim$ 400</td>
<td>1.0</td>
<td>3.2 ± 0.80</td>
<td>IPDS</td>
<td>This work</td>
</tr>
<tr>
<td>(10)</td>
<td>SO$_2$' (a $\Delta^3\Pi$, $v = 3$) + N$_2$O + SO$_2$ + N$_2$O$^+$</td>
<td>323</td>
<td>0.6$^a$, 0.28</td>
<td>6.4$^a$, 0.54</td>
<td>IPDS</td>
<td>This work</td>
</tr>
</tbody>
</table>

*Selected ion flow tube with electric drift field added. Ions produced by electron impact.

$^a$Ions produced by photoionization in radio frequency ion guide, then beamed through a scattering cell filled with neutral reactant.

$^b$From measurement of fluorescence decay rate as function of pressure of quenching gas.

$^c$Threshold electron–secondary ion coincidence technique, with mass analysis of products from reaction of ion beam with neutral gas. $k_{q2}$ is derived from a cross section calculated using the theoretical method of Rapp and Frainces. (Ref. 39).

$^d$Ion photodissociation spectroscopy. The $KE_{cn}$ shown is an average value; the full range of values for ions formed in our ion source is $KE_{cn} = O - 1.54$ eV when $Q = \text{SO}_2$ and $O = 1.16$ eV when $Q = \text{N}_2$.}

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[References]

15. The "330" in reaction (26) means $v_1=3$, $v_2=3$, $v_3=0$ quanta in the three vibrational modes of SO$_2^*$, and so forth through subsequent reactions.


END