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Charge transfer between the $2p^2\,^3P$ ground-state O^{2+} ion and He, H_2, N_2, and CO at electron-volt energies

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The charge-transfer rate coefficients for the reaction $O^{2+}(2p^2\,^3P)$ + He, H_2, N_2, and CO $\rightarrow$ products are measured at energies about 2.5 eV using a laser-induced-plasma ion source and ion storage. The rate coefficients are $1.12(0.15)\times10^{-12}$ cm^3 s^{-1}, $2.36(0.22)\times10^{-9}$ cm^3 s^{-1}, $3.15(0.26)\times10^{-9}$ cm^3 s^{-1}, and $3.40(0.29)\times10^{-9}$ cm^3 s^{-1}, respectively. While our result for O^{2+} and H_2 is consistent with the published value, the charge-transfer rate coefficient for O^{2+} and He disagrees with all the available theoretical and experimental values by as much as three orders of magnitude. No theoretical value is available for $O^{2+} + N_2$. However, our measured value at 2×10^4 K is different from that obtained by the drift tube method at 300 K by a factor of 2. No theoretical and experimental values are available for comparison for the charge-transfer reaction of O^{2+} and CO.

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I. INTRODUCTION

Charge-transfer processes between multiply charged ions and neutral atoms and molecules are of considerable interest in astrophysics, plasma physics, and for verifying basic theoretical treatments in low energy collisions. The O^{2+} ions are of particular interest since they are abundant in the terrestrial ionosphere, in supernovas, and in the upper atmospheres of Mars and Venus [1], and in the upper atmospheres of Earth [2]. Their electron-transfer collisions with He, H_2, and N_2, at mean collision energies of a few eV or less, often play important roles in the formation and destruction of ions related to them. However, our recent charge-transfer measurement of O^{2+} and He [3] differs significantly from the calculations of Dalgarno *et al.* [1] and Gargaud *et al.* [4]. In this paper, we will reexamine our results, and will provide additional evidence to support the result of our previous measurements of the $2p^2\,^3P$ ground-state O^{2+} ion and He. Furthermore, we will present charge-transfer results of the O^{2+} ($2p^2\,^3P$) ion and H_2, N_2, and CO at electron-volt energies using laser ablation and the ion trap storage technique.

II. EXPERIMENTAL METHOD

The measurements of the ground-state thermal energy charge-transfer rate coefficient between O^{2+} ions and molecules are carried out by using a technique which combines a laser ablation ion source and ion storage. With this technique, ions are produced from a solid target, and no source gas is required. This eliminates the potential source of systematic error due to reactions between ions and the source gas. The mass selectivity of the ion trap enables us to store a specific ion group for study with no other concomitant ions present.

The facilities used in this experiment have been described in detail earlier [5,6]. Briefly, O^{2+} ions are produced by laser ablation of solid ferric oxide (Fe_2O_3) targets. We used the output of the second harmonic (532 nm) of a pulsed Nd:YAG laser (Molectron MY-34) as an ablation source. In this series of measurements, approximately 0.3 mJ of the second harmonic of the Nd:YAG laser was used. The power density was estimated to be about 10 MW cm^{-2}. The low power density of the ablation source eliminates the formation of higher charge states of iron and oxygen, which can be stored simultaneously with O^{2+} ions in the trap. The trapping parameters (rf frequency $f = 1.4$ MHz, amplitude $V_0 = 380$ V, and dc bias $U_0 = 35$ V) of the rf quadrupole ion trap were chosen to selectively store O^{2+} ions. Lower charge states of iron and oxygen ions were excluded from the trap. The number of O^{2+} ions stored in the trap was about 10^3, and the mean energy of the ion was estimated to be about 2.5 eV (2×10^4 K) [3,7]. The storage time ($1/e$) was in excess of 10 s at a base vacuum pressure of 5×10^{-10} Torr. The charge-transfer rate measurements were performed by measuring the relative number of O^{2+} ions remaining in the trap, as a function of time, after they were stored in the presence of a neutral gas of known density. The O^{2+} ions were extracted from the trap and their relative number was measured by a 0.3-m time-of-flight (TOF) mass spectrometer equipped with an electrostatic lens and a 1-in.-diameter dual microchannel plate.

In all the measurements, neutral gases with a minimum of ultrahigh-purity grade were used. These gases include He (Linde, ultrahigh purity, 99.999%), H_2 (Alphagaz, ultrahigh purity, 99.999%), N_2 (Airco, ultrahigh purity, 99.999%), and CO (Alphagaz, research, 99.97%). The neutral gas was introduced into the vacuum chamber through a gas handling system. To minimize contamination during the transfer of the gas into the vacuum chamber, the reservoir of the gas handling system was evacuated to $\sim10^{-2}$ Torr through a cold trap with a mechanical pump. The reservoir was then flushed with

10^3 Torr of the neutral gas. This flushing procedure was repeated at least five times to ensure minimal contamination of the neutral gas. A leak valve between the reservoir and the vacuum chamber controlled the flow rate of the neutral gas into the vacuum chamber, thus providing a fine control of the neutral gas pressure in the vacuum chamber. The pressure of the neutral gas was measured by a calibrated ion gauge. The calibration procedure was discussed in a previous publication [5]. The purity of the neutral gas in the vacuum chamber was confirmed by a quadrupole mass analyzer. We shall discuss the procedure to confirm the purity of the He gas in Sec. IV.

In our measurement of H_2 and N_2, we introduced a procedure to measure the decayed ion signal as a function of the storage time. While the procedure used in our previous measurements [3,5,8] provides adequate ion signals, the new approach minimizes both the short-term and the long-term ion signal fluctuation and drift caused by the instability of laser power and the changing surface condition of the target, when the ablation laser gradually drills into the target surface. An outline of the procedure is in the following paragraph.

The ion signals are measured, alternately, at a delay time t and at the shortest delay time $t_0 = 0.4$ s. Each pair of measurements consists of 20 laser shots and more than ten such pairs of measurements are made for each time t. The intensity ratio $I_r = I_t/I_{t_0}$ is computed to obtain a normalized relative intensity. The storage time is then scanned at a later time t with a time increment δt to obtain the ion decay curve.

We compared the decay constants obtained using this approach with that used in previous measurements [3,5,8]. While there is no noticeable difference in the decay constants obtained in either method, the new procedure gives a significantly smaller statistical uncertainty.

III. CONFIRMATION OF THE PRODUCTION AND THE STORAGE OF $2p^2\,{}^3P$ GROUND-STATE O^{2+} IONS

O^{2+} ions produced by laser ablation can be in a variety of excited electronic states immediately after they are produced. Rapid cascade from these highly excited electronic states, through allowed transitions and collisional deexcitations of the excited states by plasma electrons, leaves O^{2+} ions in their low lying metastable states, such as $2p^2\,{}^1D$ with a mean lifetime of 37 s [9], and the $2p^2\,{}^3P$ ground state during the early expansion phase into the vacuum. The ratio of the number of metastable-state ions to ground-state ions depends on the density and the temperature of the plasma electrons during the self-similar expansion of the plasma in the vacuum chamber [10]. The electron time-of-flight data obtained from a Langmuir probe, mounted at a known distance from the ion trap, allowed us to estimate the electron density and temperature at the early phase of the plasma expansion. The result of the estimation led us to the conclusion that the stored O^{2+} ions are in their ground states [3].

We have confirmed the electronic state of the stored O^{2+} ions by measuring their charge-transfer rate coefficient with H_2, and compared that with the known charge-transfer rate coefficients for the ground and the metastable O^{2+} ions [6]. The charge-transfer rate coefficients for molecular hydrogen with the $2p^2\,{}^3P$ ground-state O^{2+} ion and the long-lived $2p^2\,{}^1D$ metastable-state O^{2+} ion are 1.71×10^{-9} cm^3 s^{-1} and 9.6×10^{-9} cm^3 s^{-1}, respectively, using a Penning trap at the mean energy of 1.25 eV [9].

Figure 1(a) shows the TOF mass spectrum of laser-produced O^{2+} ions stored in the trap. In the same figure, the TOF mass spectrum of the ions produced by electron impact dissociative ionization of N_2 and CO gas is also included for calibration purposes. Only O^{2+} ions are stored in the trap. Figure 2 shows typical decay curves of the O^{2+} ion signal versus storage time at five different pressures of H_2. The decay of the ion signal can best be fitted by a single exponential function, indicating that O^{2+} ions exist in one state. The rate coefficient obtained from the slope of the decay rate at five different H_2 densities is $2.36(0.22) \times 10^{-9}$ cm^3 s^{-1} (see Fig. 3). This rate coefficient is within 30% of the value measured by Church and Holzscheiter [9] for the $2p^2\,{}^3P$ ground state of O^{2+} ions. This clearly indicates that the stored O^{2+} ions are in the ground state.

IV. MEASUREMENT OF O^{2+} IONS AND He

A recent calculation by Gargaud *et al.* [4] gives a rate coefficient of 1.01×10^{-9} cm^3 s^{-1} at 2×10^4 K. This value is about three orders of magnitude higher than the value reported in our recent measurement at similar energies. In view of this, we have carried out additional measurement to test our results.

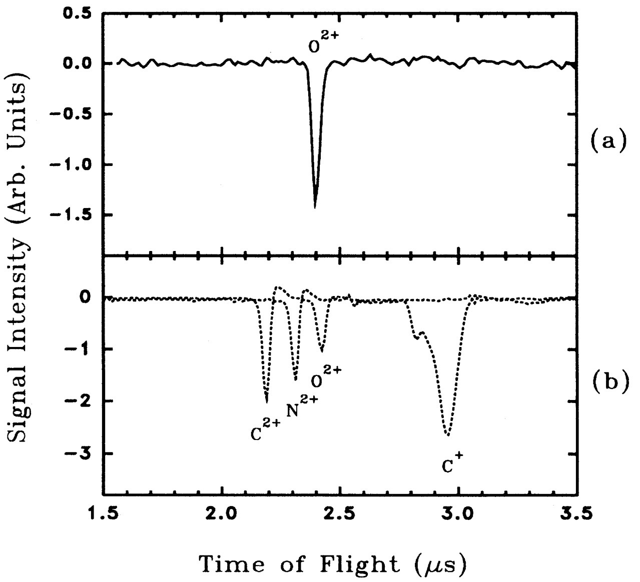

FIG. 1. (a) A time-of-flight mass spectrum of laser-produced O^{2+} ions stored in a rf trap. (b) A time-of-flight mass spectrum of ions produced by electron impact of N_2 and CO.

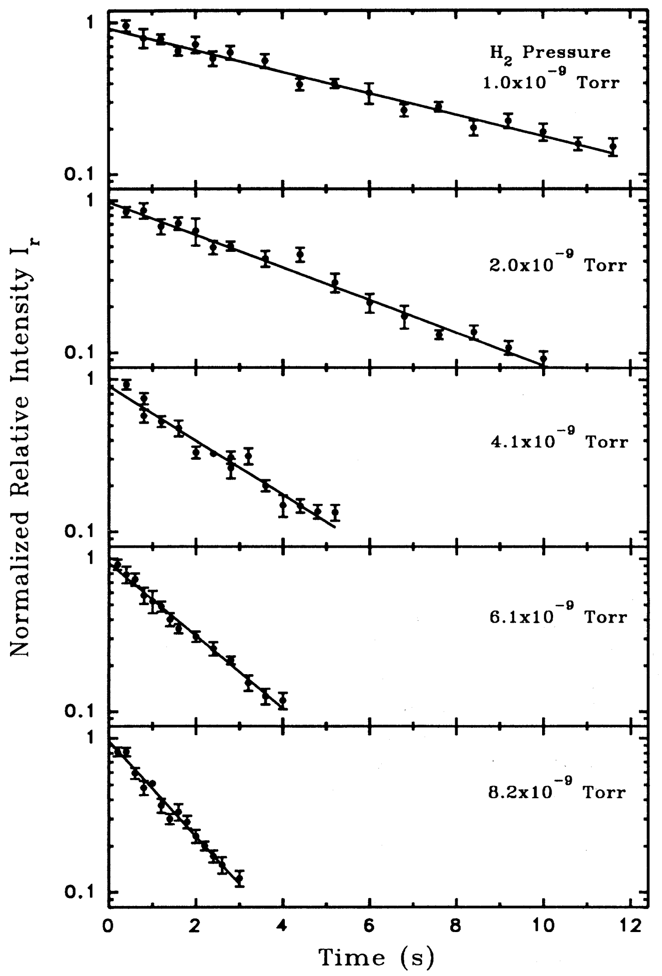

FIG. 2. The decay curves of normalized relative intensity of O^{2+} ion vs storage time at five different pressures of H_2. Each data point represents about 130 measurements. The uncertainty (1σ) is due to the statistical fluctuation of the ion signal. Solid lines are the least-squares fits to a single exponential function.

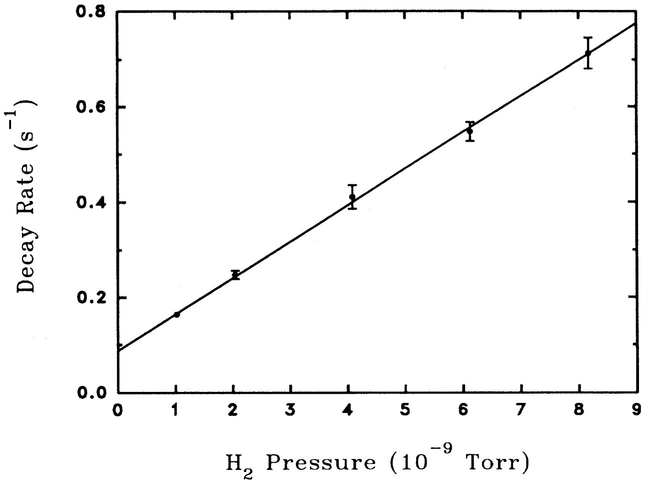

FIG. 3. O^{2+} ion decay rate vs H_2 pressure. Each error bar represents the statistical uncertainty of 1σ. The slope of the straight line fit gives the charge-transfer rate coefficient of the O^{2+} ion with H_2.

If the charge-transfer rate coefficient for the ground-state O^{2+} ion and He is as high as 10^{-9} $cm^3\,s^{-1}$, then even at the lowest He pressure of 0.5×10^{-6} Torr used in our recent measurement [3], nearly all the ground-state O^{2+} ions would have captured electrons and would have left the trap within 0.4 s after the O^{2+} ions were created and stored in the trap. Those O^{2+} ions that were left behind in the trap and reacted slowly with He should have been in their low lying metastable states. The only metastable state that can survive for 0.4 s or more in the trap must be the long-lived $2p^2\,{}^1D$ metastable state of O^{2+} ions. This argument, however, contradicts the result of our previous experiment with H_2; i.e., all O^{2+} ions are in their $2p^2\,{}^3P$ ground state [6].

We have performed further tests to determine if the rapid charge-transfer rate of 10^{-9} $cm^3\,s^{-1}$ exists for the O^{2+} + He reaction. If we assume such a rate coefficient, then at a He pressure of 5×10^{-8} Torr the mean charge-transfer collision time is about 0.6 s. We should be able to detect a significant drop in the ion signal due to such a fast reaction rate. We have eliminated the change in the ion signal caused by the residual gases in the vacuum chamber by comparing the O^{2+} ion signal intensity in the presence of 5×10^{-8} Torr of He and with He pumped out of the system. Figure 4 shows the ratio of O^{2+} ion signal intensities with 5×10^{-8} Torr of He and without He at a delay time of 0.4 s, 1 s, and 2 s after the ions are stored in the trap. The invariance of the differential ion signals over two seconds indicates that a rapid charge-transfer rate with He does not exist.

Since the charge-transfer rate between the ground-state O^{2+} ion and helium may be several orders of magnitude smaller than that of molecular gases, the purity

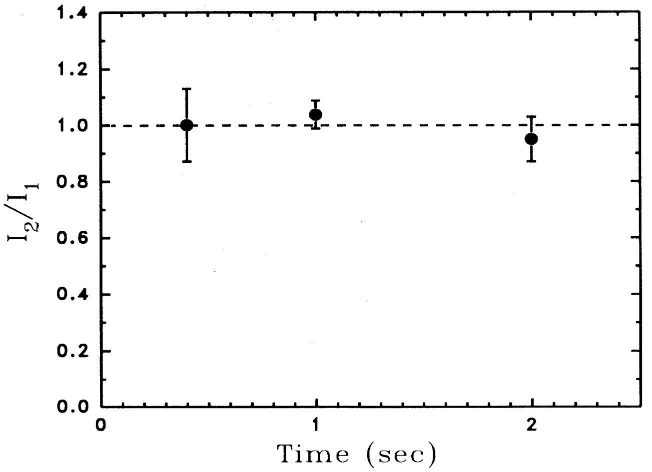

FIG. 4. The ratio of the O^{2+} ion signal, I_2, at 5×10^{-8} Torr of He and the O^{2+} ion signal, I_1, with He pumped out of the vacuum chamber at 0.4 s, 1 s, and 2 s after O^{2+} ions are stored in the trap. The horizontal dotted line indicates the intensity ratio of 1.

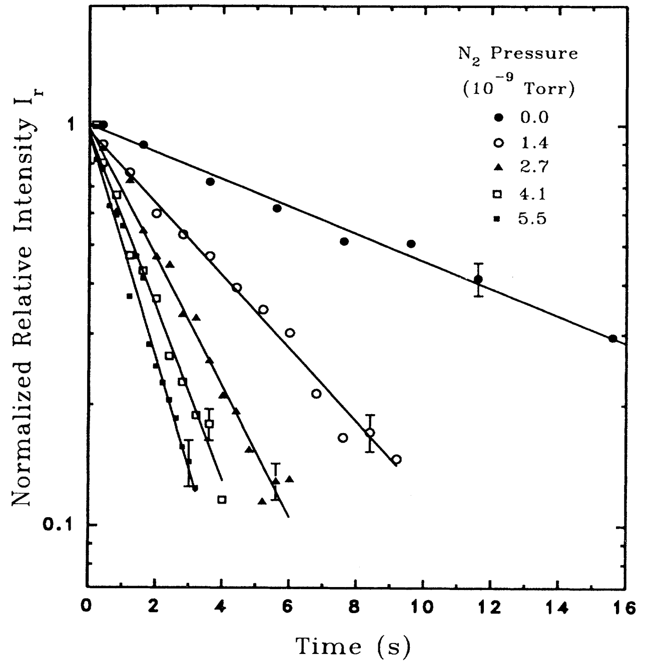

FIG. 5. The decay curves of the normalized relative intensity of O^{2+} ions vs storage time at five different pressures of N_2.

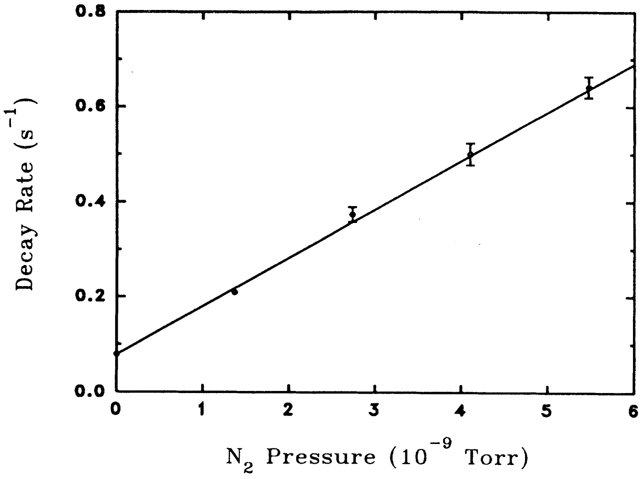

FIG. 7. O^{2+} ion decay rate vs N_2 pressure.

of the helium gas admitted into the reaction chamber is very critical to the accuracy of the measurement. The presence of a minute amount of impurity gas, such as O_2, N_2, or CO, that has a charge-transfer rate of the order of $\sim 10^{-9}$ $cm^3\,s^{-1}$, can cause a significant systematic error to the measurement. The purity of the He gas has been examined carefully in the vacuum chamber using a quadrupole mass analyzer (Masstorr DX100). First, the residual gas in the vacuum chamber was mass analyzed. The residual gas was composed mainly of H_2 (2 amu), H_2O (18 amu), CO and/or N_2 (28 amu), and a small amount of CO_2 (44 amu). The amount of the CO and/or N_2 component is about 1/3 of the total residual gas. Second, we introduced 2.5×10^{-6} Torr of ultrahigh-purity helium gas from the gas handling system. The mass spectrum showed a noticeable increase only in the mass 28 amu component by about 20%. This corresponds to a pressure increase of 3.5×10^{-11} Torr. A much smaller increase was also observed in the CO_2 component. The total impurity of the helium gas admitted into the vacuum chamber is therefore about 15 ppm. This value is close to the limit specified by the ultrahigh-purity helium (99.999%) used in the measurement. Nevertheless, the impurity causes a systematic error of about 5% in the measurement. The quadrature sum of all the errors gives a total uncertainty of 13.5%.

Since there is no evidence that the charge transfer between He and the ground O^{2+} ion is rapid, and the purity of the He gas is confirmed, we have no reason to doubt our previous result [3]. However, we made a minor adjustment in the uncertainty of the previous result to include the effect caused by the presence of 15 ppm of impurities in the ultrahigh-purity helium gas used.

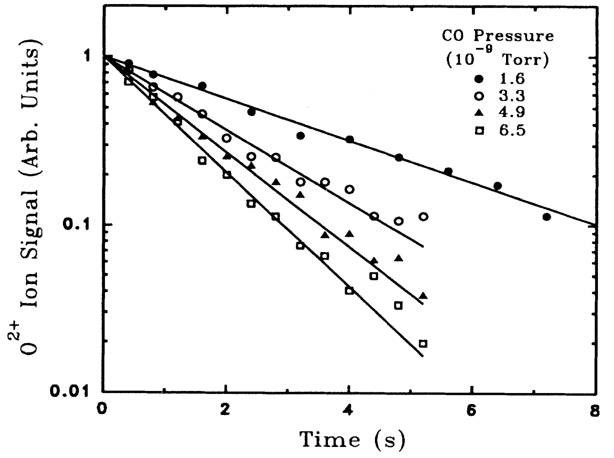

FIG. 6. The decay curves of the O^{2+} ion signal vs storage time at four different CO pressures.

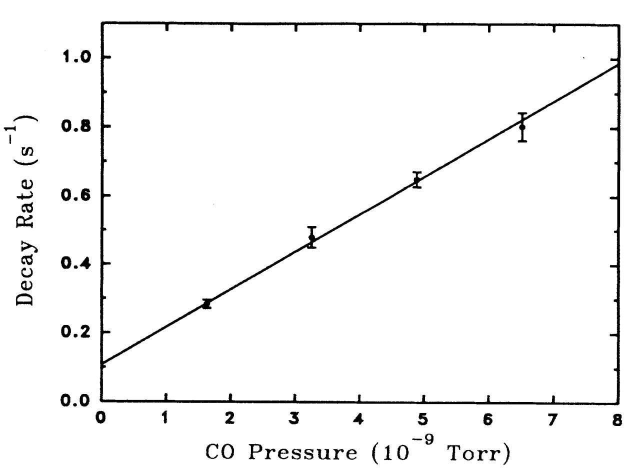

FIG. 8. O^{2+} ion decay rate vs CO pressure.

TABLE I. Measured and calculated charge-transfer rate coefficients K for O^{2+} with He, H_2, N_2, and CO.

Reaction	Reference	K ($cm^3\,s^{-1}$)	Temperature (K)	Method
O^{2+} + He	[12]	$\leq 10^{-14}$	3×10^2	Experiment, drift tube
	[13]	$3.5(1.5) \times 10^{-11}$	4×10^2	Experiment, drift tube
	[14]	2×10^{-11}	4×10^2	Theory, distorted wave
	[1]	10^{-14}	3×10^2	Theory, quantal calculation
		4×10^{-14}–4×10^{-13}	1×10^3	
		2×10^{-11}–1×10^{-10}	1×10^4	
	[15]	8×10^{-12}	3×10^2	Theory, quantal calculation
		1.0×10^{-10}	5×10^3	
		2.0×10^{-10}	1×10^4	
		3.9×10^{-10}	2×10^4	
		5.9×10^{-10}	3×10^4	
		8.9×10^{-10}	5×10^4	
	[4]	0.7×10^{-10}	2×10^2	Theory, quantal calculation
		1.3×10^{-10}	5×10^2	
		1.01×10^{-9}	2×10^4	
	[3]	$1.12(0.15) \times 10^{-12}$	2×10^4 [a]	Experiment, ion trap
O^{2+} + H_2	[9]	$1.71(0.15) \times 10^{-9}$	1×10^4 [b]	Experiment, Penning trap
	[6]	$2.36(0.22) \times 10^{-9}$	2×10^4 [a]	Experimental, Paul trap
O^{2+} + N_2	[11]	$1.3(0.3) \times 10^{-9}$	3×10^2	Experimental, drift tube
	This work	$3.15(0.26) \times 10^{-9}$	2×10^4 [a]	Experimental, Paul trap
O^{2+} + CO	This work	$3.40(0.29) \times 10^{-9}$	2×10^4 [a]	Experimental, Paul trap

[a] Estimated from $\bar{E} = \frac{3}{2}kT$ with $\bar{E} \approx 2.5$ eV. Previous measurements in a rf trap indicate that the ion energy distribution is approximately thermal [7].

[b] Also estimated from the mean energy, which is $\bar{E} = 1.25$ eV, given in Ref. [9].

The rate coefficient for ground-state O^{2+} ions and He is $1.12(0.15) \times 10^{-12}$ $cm^3\,s^{-1}$.

V. MEASUREMENT OF O^{2+} IONS AND N_2 AND CO

Measurements were also carried out for the charge transfer between ground-state O^{2+} ions and N_2 and CO. In both cases, ultrapure grade N_2 and CO gases were used. The purity of these gases was confirmed using the same procedure described above. The charge-transfer rate coefficient (K) is derived using the same procedure as before; i.e., from the slope of the ion decay rate ($1/T$) vs gas density (P):

$$\frac{1}{T} = \frac{1}{T_0} + KP, \qquad (1)$$

where $\frac{1}{T_0}$ is the charge-transfer rate coefficient of O^{2+} ions and the residual gas in the vacuum chamber ($\sim 5 \times 10^{-10}$ Torr). Figures 5 and 6 show the O^{2+} ion intensities as a function of storage time for N_2 and CO, respectively, at different gas pressures. The solid lines represent the least-squares fits of the data to a one-exponential function. The monotonic decrease in the collisional rate with decreasing target gas pressure is shown in Figs. 7 and 8. The slopes in the figures are obtained by a weighted least-squares fit to a linear function according to Eq. (1). The rate coefficients for ground-state O^{2+} ions and N_2 and CO are $3.15(0.26) \times 10^{-9}$ $cm^3\,s^{-1}$ and $3.40(0.29) \times 10^{-9}$ $cm^3\,s^{-1}$, respectively. The estimated uncertainty of the result is mainly due to the uncertainty in the statistical fluctuation of the ion signals (typically about ±2.5%) and the uncertainty in the estimation of the target gas density (±8%) [5]. While there are no available data for comparison with our CO measurement, our value for N_2 differs by a factor of 2 from results obtained using a drift tube at lower energies [11].

VI. SUMMARY AND RESULTS

Table I summarizes the results of various calculations and measurements. While our results for O^{2+} and H_2 are consistent with published values, our measured value for O^{2+} ions and He disagrees by as much as three orders of magnitude with the most recent calculation. Neither theoretical nor experimental values for CO are available for comparison. We hope that these measurements will stimulate further refinement of theoretical treatments, and improve the accuracy of charge-transfer measurements at electron-volt energies [16].

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