

## Mobility of O<sup>+</sup> in He and interaction potential of HeO<sup>+</sup>

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New experimental measurements are reported for the mobility of O<sup>+</sup> ions in He gas at 300 K. The accuracy of these new values is estimated as  $\pm 2.5\%$ , which allows them to serve as a stringent test of a new *ab initio* potential that we have calculated using the RCCSD(T) method. We employed the aug-cc-pV5Z basis set with counterpoise corrections and took spin-orbit coupling into account. The present experimental values lie below the calculated ones, but the difference becomes statistically significant only at moderate and high values of the ratio of the electric field strength to the gas number density; even there they are only marginally significant. © 2006 American Institute of Physics. [DOI: 10.1063/1.2337634]

### I. INTRODUCTION

The reactive properties of O<sup>+</sup> ions in the gas phase are highly sensitive to the particular charge states involved.<sup>1-4</sup> Moreover, the reactions are often so rapid that accurate measurements of rate coefficients must be obtained using gas mixtures in which the main component is nonreactive, customarily a rare gas. For this reason, the transport properties of atomic oxygen cations moving through the rare gases have been of interest since 1969.<sup>5,6</sup> The various studies between then and 1987, including the work of Lindinger and Albritton<sup>7</sup> with ground-state ions and of Rowe *et al.*<sup>8</sup> with excited-state ions, were summarized by Simpson *et al.*<sup>9</sup> Unfortunately, the accuracies in the early reaction studies were often not better than 40% for rate coefficients, so errors in the ancillary transport properties were deemed acceptable even when they were as large as 10%.

The mobilities of O<sup>+</sup> in He at room temperature were measured with somewhat better accuracy by Johnsen *et al.*<sup>10</sup> in a selected ion drift apparatus. At low values of  $E/n_0$ , the ratio of the electrostatic field strength to the gas number density, three groups of oxygen ions with a mass to charge ratio of 16 could be distinguished in He. It was concluded that the ions of lowest mobility were O<sub>2</sub><sup>2+</sup>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>), possibly with vibrational excitation. The other ions were identified as O<sup>+</sup>(<sup>4</sup>S) and O<sup>+</sup>(<sup>2</sup>D). Mobilities were obtained for values of  $E/n_0$  between 0 and 200 Td (1 Td = 10<sup>-21</sup> V m<sup>2</sup>) for the <sup>4</sup>S ions and between 0 and 40 Td for the <sup>2</sup>D ions. The experimental uncertainties arising from voltage and pressure measurements in those experiments were  $\leq 1\%$ . A larger source of

error, however, was associated with the injection of the ions into the drift cell at an energy considerably in excess of the final drift energy. Although corrections for such injection effects were made, the final data may still have errors as large as 5%.

New values of the mobility of O<sup>+</sup>(<sup>4</sup>S) in He were reported in 1993,<sup>11</sup> as functions of  $E/n_0$  at a variety of gas temperatures from 93 to 568 K. Although the accuracies of the results at each temperature were still estimated at 5%, it was believed that the use of all of the data could serve to test information about the interaction potential almost as well as having data of greater accuracy at a single temperature. It was noted that the data at 93 K did not match smoothly with the data at higher temperatures obtained in the same apparatus, and that there was a systematic difference of about 4% between the new values at room temperature and those obtained previously. One purpose of the present work is to further improve the accuracy of the mobility of O<sup>+</sup>(<sup>4</sup>S) ions in He gas at room temperature, as a function of  $E/n_0$ .

The various interaction potentials for the HeO<sup>+</sup> system that had been reported by 1987 were summarized by Simpson *et al.*<sup>9</sup> Included was the empirical potential of Viehland and Mason<sup>12</sup> obtained by choosing parameters that would allow the  $(n, 6, 4)$  functional form for the potential to match the dependence upon  $E/n_0$  of the experimental mobilities.<sup>7</sup> The best match was with  $n=8$ , for which the potential minimum had a value of 2.00 mhartree at an internuclear separation of 4.06 bohr. Although this information is about some average potential that represents the behavior of O<sup>+</sup> ions in a mixture of low-lying states, it was sufficiently accurate to allow thermal rate coefficients for O<sup>+</sup> reactions at elevated

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temperatures to be extracted from swarm measurements of the rate coefficient at low temperatures and high  $E/n_0$ .

The ground state of  $\text{HeO}^+$  is the  $4\Sigma^-$  state that separates at infinity into  $\text{He}(1S)$  and  $\text{O}^+(4S)$ . The potential energy curve for this state was calculated by Simpson *et al.*<sup>9</sup> at the MP4SDQ/6-311+G(3df,3pd) level of theory, excluding core contributions to the correlation energy. This potential had a well depth of 1.42 mhartree at an ion-neutral separation of 4.57 bohr. It is probably more accurate than the MP4SDTQ/6-311+G(2df,2pd)//MP2/6-31G(d,p) potential that Frenking *et al.*<sup>13</sup> obtained later using a smaller basis set, which had a well depth of 1.27 mhartree at 4.67 bohr. The potential of Simpson *et al.*<sup>9</sup> was consistent with the experimental mobilities, but only because the error bars on the experimental data existing in 1987 were large. The agreement of results calculated from this potential with the 1993 data<sup>11</sup> was “not excellent,” but within the combined uncertainties of the measurements and calculations.

Adiabatic potentials for the lowest states of  $\text{HeO}^+$  were obtained in 1994 (Refs. 14 and 15) by multireference single- and double-excitation configuration interaction using a  $(9s4p1d)/[7s3p1d]$  basis set for helium. For oxygen, the basis set was  $(9s5p1d)/[5s3p1d]$  which is a double  $\zeta$  plus polarization basis set with added diffuse  $s$ ,  $p$ , and  $d$  orbitals. Unfortunately, the resulting potential energy curves were presented only graphically, and no quantitative results were reported for the positions and depths of the wells for the various molecular states. However, spin-orbit and nonadiabatic couplings were considered in determining cross sections for electron capture by  $\text{O}^+$  ions colliding with helium at impact energies from 160 eV to 9 keV, and good agreement was found with experimental data when provision was made for a significant presence of  $\text{O}^+$  ions in the  $2D$  and  $2P$  states.

In 2001, potential energy curves for several states of  $\text{HeO}^+$  were determined<sup>16</sup> by the complete active space self-consistent field (CASSCF) method using triple  $\zeta$  plus polarization basis functions, i.e.,  $(7s3p2d)/[4s3p2d]$  for helium and  $(11s6p3d2f)/[5s4p3d2f]$  for oxygen. The  $4\Sigma^-$  state was found to have a well depth of 1.067 mhartree at 4.52 bohr, and it supported four discrete vibrational levels. The focus of that work was prediction of the fluorescence spectrum and the possibility of lasing action in this system, and no direct comparisons were made with experimental results.

Multireference configuration interaction calculations with correlation consistent basis sets were used in 2004 (Ref. 17) to determine the potential energy curves for low-lying electronic states of  $\text{HeO}^+$ . Since the focus of that work was properties of  $\text{HeO}^+$  that are important for its role as a constituent in the fragmentation of  $\text{He}_2\text{O}^{2+}$ , no attempt was made to determine accurate values for the well depth of the diatomic ion, and the potential energy curves were given only in graphical form.

Recently we have been generating accurate potential energy curves for a large number of systems. Our work with closed-shell cations was described in the introduction of a paper<sup>18</sup> concerning an open-shell anion ( $\text{O}^-$ ) moving through He, Ne, and Ar. In the latter cases, three low-lying states had to be considered with full counterpoise correction, and spin-orbit effects had to be included in order to match the avail-

able spectroscopic and transport data. Similarly careful treatment has recently been reported for the open-shell  $\text{Hg}^+$  and  $\text{Cd}^+$  ions in the rare gases from He to Rn<sup>19</sup> and for  $\text{S}^-$  in He.<sup>20</sup> The present work concerning  $\text{HeO}^+$  is an extension of these efforts.

In Sec. II we describe the new experimental work. The new calculations are reported in Sec. III. The experimental and theoretical results are compared to each other and to prior results in Sec. IV. Section V contains a discussion of the accuracies of both the new experimental values and the new interaction potential.

## II. EXPERIMENTAL DETAILS

The Pittsburgh selected ion drift apparatus (SIDA) was first described in 1982,<sup>10</sup> when it was used to study the mobilities of ground-state and metastable  $\text{O}^+$  and  $\text{O}_2^{2+}$  ions in helium. A short description of this instrument has also been given in the book by Mason and McDaniel.<sup>21</sup> The SIDA consists of an ion drift tube with length of 35.66 cm, a pulsed electron-impact ion source, and two differentially pumped quadrupole mass filters. The “injection mass filter” serves to remove ions of the wrong mass-to-charge ratio from those produced in the ion source, and injects the correct ions through a small entrance orifice into the drift tube proper. After an ion pulse, containing typically from  $10^5$  to  $10^6$  ions, has traversed the drift tube, a small fraction of the ions passes through a sampling orifice into the “analyzer mass filter” that separates the injected ions from products of ion molecule reactions that may have occurred in the drift section. Finally, the ions are detected by a means of continuous-dynode particle multiplier whose output pulses after electronic processing are coherently summed in a digital time-of-flight analyzer. The instrument has been in frequent use over the years, but primarily for the purpose of studying ion-neutral reactions and dissociative recombination, where minor errors in the mobility of the ions are unimportant. Only insignificant modifications have been made since the work described in 1990 (Ref. 22) on mobilities of  $\text{He}^+$  ions in Ne.

While measurements of ion mobilities are basically rather simple, there are several sources of uncertainties that reduce the accuracy of the resulting data. The quantities that enter into the analysis are (a) the gas pressure and temperature, (b) the electric field strength, (c) the effective length of the drift tube, and (d) the measured ion transit time. In this work, we have attempted to minimize the errors as much as could be done with the existing equipment. Instead of calibrating the capacitance manometer by comparison to an external standard, we remeasured the very precisely known<sup>23</sup> mobility of atomic neon ions in neon. This measurement revealed that the reading of our capacitance manometer had drifted downward by  $7 \pm 0.5\%$ . All later pressure readings were corrected accordingly. The gas temperature was carefully measured and did not deviate by more than 1 from 300 K at any time. The average electric field strength should be accurate to better than 0.5% while local deviations from the average field strength are estimated to be less than 0.2%. The measured ion transit times, after correcting for the small

but finite transit times in the mass filters and for electronic processing delays, are subject to random errors due to counting statistics but should be free of significant systematic errors.

The largest source of error is due to the “injection effect,” by which term we mean the effects that arise because the ions are injected into the drift region with 20–100 eV of excess kinetic energy and so penetrate a significant distance (several millimeters at a helium pressure of 1 Torr to several centimeters at 0.1 Torr) into the drift tube before assuming the equilibrium drift velocity. It is difficult to correct for this effect in a drift-tube mass spectrometer of fixed length. If left uncorrected, the apparent mobilities show an unphysical inverse dependence on gas density for a given value of  $E/n_0$ . We observed this when we attempted to measure the mobility of O<sup>+</sup> ions in He by injecting the ions directly into helium. In comparison, such effects were hardly noticeable in measurement of the mobility of O<sup>+</sup> ions in neon and argon to be reported in a later paper. As might be expected, the larger O<sup>+</sup>/He mass ratio makes the thermalization less efficient in helium than in the heavier gases. A further technical problem arose from oxidation of ion source surfaces; it was found that after a short period of operation in oxygen the extraction voltages had to be increased which made the injection effects worse.

To circumvent the injection effects, we decided to inject He<sup>+</sup> ions into the drift tube filled with helium and a minute addition of oxygen (less than 0.01%). The dissociative charge transfer reaction



is known<sup>1</sup> to produce about 2/3 of the O<sup>+</sup> ions in the <sup>4</sup>S state and 1/3 of them in the low-lying <sup>2</sup>D (or perhaps <sup>2</sup>P) state. Since the mobility of He<sup>+</sup> ions in helium is far smaller than that of O<sup>+</sup> ions, the charge transfer reaction produces an O<sup>+</sup> arrival spectrum that extends from the shorter transit time of O<sup>+</sup> ions to the longer transit time of He<sup>+</sup> ions. The onset of the arrival spectrum has the shape of two superimposed but slightly displaced error functions from which the mobilities of O<sup>+</sup>(<sup>4</sup>S) and O<sup>+</sup>(<sup>2</sup>D) can be deduced by curve fitting, as shown in the paper by Johnsen and Biondi.<sup>1</sup> This indirect procedure of determining the mobility of O<sup>+</sup>(<sup>4</sup>S) from the He<sup>+</sup>-generated arrival spectrum has the advantage that it is essentially free of injection effects, since the injected He<sup>+</sup> ions undergo symmetric charge transfer with the abundant helium atoms and lose both momentum and excess kinetic energy in one or two collisions. The O<sup>+</sup> product ions are formed with only the small energy of dissociation and separate with nearly isotropic initial velocities. Test measurements confirmed the absence of injection effects when this method was used. From these measurements, we estimated that the uncertainty introduced by indirectly determining the mobility of O<sup>+</sup>(<sup>4</sup>S) in He is on the order of ±1%, if the fraction of O<sup>+</sup> ions produced in the various states is accurately known.

There are four estimates in the literature for the branching ratio of Eq. (1) to produce O<sup>+</sup>(<sup>4</sup>S). An estimate of 95% was obtained<sup>24</sup> using 2 eV He<sup>+</sup>, but this value is unlikely to apply to the near-thermal energies employed here. The esti-

mates for thermal He<sup>+</sup> are 62.5%<sup>25</sup> and 64%.<sup>1,26</sup> A measured (but unreported) thermal value of 63% was used in connection with more recent work<sup>10</sup> with the Pittsburgh SIDA, and that is the value we used to obtain the mobility values reported below. In order to ascertain the effect that this parameter has on the mobilities we obtain, we also made calculations with branching ratios of 2/3 and 60%, and observed a maximum mobility difference of 0.78%. Hence we expect that the values reported below have a total inaccuracy of not more than 2.5%, based on 0.5% for the branching ratio differing from 63%, 1.0% for the uncertainty introduced by extracting the O<sup>+</sup> mobilities indirectly from the rather involved arrival-time spectrum, and 1.0% for the measurements of the pressure, temperature, and electric field strength.

Clustering of O<sup>+</sup> to helium has a completely negligible effect on the measured mobilities since, as a consequence of the very weak binding of O<sup>+</sup> to helium, the clustering-breakup equilibrium at room temperature will be almost entirely on the side of unclustered O<sup>+</sup> ions. Three-body association of O<sup>+</sup> with O<sub>2</sub> is very slow at the low experimental O<sub>2</sub> concentrations, and any association complexes thus formed would decay by charge transfer, forming O and O<sub>2</sub><sup>+</sup>, rather than by dissociation back into O<sup>+</sup> and O<sub>2</sub>. However, in the course of this work we noticed another possible source of error. It occasionally happened that the value of  $E/n_0$  in the drift tube was accidentally raised above the threshold for gaseous breakdown. While this caused no permanent damage to the instrument, the mobility data taken after such events were typically several percent lower than those taken before the breakdown. The effect may be due to residual surface charges that remained on the drift tube electrodes for several hours. All such data were discarded.

All of the present mobility data shown were obtained by injecting He<sup>+</sup> ions. As illustrated in Fig. 1, the data above 11 Td show no dependence upon number density except through  $E/n_0$ , but the scattering of the values becomes unacceptably large below 11 Td. We therefore smoothed the 84 mobility values in two ways. First, the values were fit to a power series of the form

$$\frac{K_0(E/n_0)}{1 \text{ cm}^2/\text{V s}} = \sum_{i=0} c_i \left[ \ln \left( \frac{E/n_0}{1 \text{ Td}} \right) \right]^i, \quad (2)$$

stopping after the term with  $i=8$  because including more terms led to a poorer statistical fit. At low  $E/n_0$ , Eq. (2) is equivalent to an expansion of  $K_0$  in powers of  $E/n_0$  which is known<sup>21</sup> to be correct at low  $E/n_0$ . The advantage of the logarithmic fit used here is that it does not have the small radius of convergence<sup>21</sup> that restricts an expansion in powers of  $E/n_0$  to values below about 30 Td. The second fitting procedure used the six-parameter functional form,<sup>27,28</sup>

$$\begin{aligned} K_0(E/n_0) = & K_0 [1 + b_1(E/n_0)^2]^{1/4} [1 + b_2(E/n_0)^2 \\ & + b_3(E/n_0)^4]^{-1/4} [1 + a_1(E/n_0)^2 \\ & + a_2(E/n_0)^4]^{-1/8}. \end{aligned} \quad (3)$$

The parameters for Eqs. (2) and (3) are collected in Table I. Statistical tests indicate that the best results are obtained when Eq. (2) is used between 11 and 27 Td and between 45

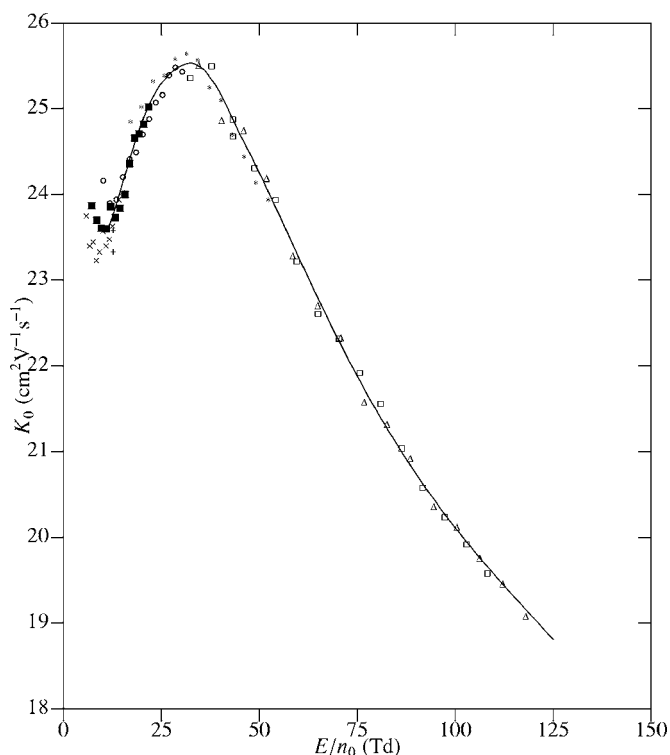


FIG. 1. Standard mobility of  $O^+(^4S)$  ions in He gas at 300 K, as functions of  $E/n_0$  at different gas pressures: 0.15 Torr (triangles), 0.16 Torr (squares), 0.30 Torr (stars), 0.52 Torr (circles), 0.72 Torr (solid squares), and 1.04 Torr (two data sets, represented by plus and multiply signs). The curve represents the present, smoothed experimental values, as given by Eqs. (2) and (3).

and 125 Td, and when Eq. (3) is used between 27 and 45 Td; neither equation should be used outside these limits.

Tables giving both the original and smoothed data have been incorporated into the gaseous ion transport database<sup>29</sup> maintained at Chatham College.<sup>30</sup>

### III. THEORETICAL DETAILS

As noted above,  $O^+$  has a  $^4S$  ground state, so it forms a  $^4\Sigma^-$  state when complexed to a helium atom. Since the next highest state of  $O^+$ , the  $^2D$  state, lies about 3 eV higher in energy, and since there are no low-lying electronic states of

TABLE I. Parameters for best fits of Eqs. (2) and (3) to the data in Fig. 1.

$K_0(0)$	23.481 00 $\text{cm}^2/\text{V s}$
$b_1$	$3.333\ 822 \times 10^{-4} \text{ Td}^{-2}$
$b_2$	$-8.000\ 000 \times 10^{-7} \text{ Td}^{-2}$
$b_3$	$2.033\ 235\ 6 \times 10^{-9} \text{ Td}^{-4}$
$a_1$	$-5.913\ 490 \times 10^{-4} \text{ Td}^{-2}$
$a_2$	$5.000\ 000 \times 10^{-7} \text{ Td}^{-4}$
$c_0$	12.145 089
$c_1$	10.836 734
$c_2$	4.944 304 9
$c_3$	-3.516 069 9
$c_4$	-5.421 682 5
$c_5$	5.174 534 5
$c_6$	-1.706 480 1
$c_7$	0.250 058 878
$c_8$	-0.013 790 31

He, then we expect a single-reference *ab initio* method to perform very well. As in our previous work noted above, we employ the RCCSD(T) method<sup>31</sup> in MOLPRO,<sup>32</sup> which is extremely accurate for the majority of single-reference systems. We employ the aug-cc-pV5Z basis set, which we have shown previously is able to describe the helium atom and its interactions with atomic ions; this basis set should be perfectly well suited to describing the  $\text{HeO}^+$  system. Potential energy curves were calculated point by point across a wide range of internuclear separations  $R$  spanning the short, medium, and long-range regions. The full counterpoise correction was applied at each point.

The potential energy curve for the  $^4\Sigma^-$  state constructed in this manner is, of course, obtained in the absence of spin-orbit coupling. Once spin-orbit coupling is considered, then the  $^4\Sigma^-$  state becomes  $^4\Sigma_{3/2}^-$ , and there is the possibility for this state to interact with others that have  $\Omega=3/2$ . The higher-lying  $^2D$  state yields  $^2\Pi$ ,  $^2\Delta$ , and  $^2\Sigma^-$ , with the first two having  $\Omega=3/2$  states that can interact with the  $^4\Sigma_{3/2}^-$  state. As mentioned previously, Hogreve<sup>17</sup> found that the  $^2\Delta$  and  $^2\Sigma^-$  did not cross the  $^4\Sigma^-$  state, that the  $^2\Pi$  did, but that the crossing was only far up the repulsive wall. (The interested reader should consult Fig. 5 of that paper to see the positions of the various potential energy curves without spin-orbit coupling.) The  $^2\Pi$  state will undergo an avoided crossing with the  $^4\Sigma^-$  state on that repulsive wall. Hence, we do not expect the spectroscopy of the  $^4\Sigma^-$  state to be significantly affected, but the transport properties at high  $E/n_0$  are likely to be affected. For this reason we also calculated the spin-orbit interacting  $^4\Sigma^-$  and  $^2\Pi$  states.

Spin-orbit coupling was included employing the Breit-Pauli operator<sup>33</sup> as implemented in MOLPRO.<sup>32</sup> CASSCF calculations are carried out with the RCCSD(T) energies employed as the unperturbed values for the spin-orbit calculations. The CASSCF calculations employed the frozen-core approximation. The standard aug-cc-pVQZ basis set was employed for He and O, including the  $s$ ,  $p$ , and  $d$  functions for He, and  $s$ ,  $p$ ,  $d$ , and  $f$  functions for O, all uncontracted.

In addition, we performed multireference configuration interaction (MRCI) scans for the  $^2\Sigma^-$ ,  $^2\Delta$ , and  $^2\Pi$  states near the minima of the  $^4\Sigma^-$  state. We used these energies to calculate spin-orbit curves. There was very little change in any of the spectroscopic parameters, as expected. We have selected the RCCSD(T) method since it is size consistent, whereas the MRCI method is not; in addition, there are other difficulties in the MRCI method, such as ensuring that all important states have been included across the full range of  $R$ .

### IV. RESULTS

The *ab initio* potential energy curve for the  $^4\Sigma^-$  state in the absence of spin-orbit coupling, and the resulting curve after interaction with the  $\Omega=3/2$  component of the  $^2\Pi$  state differ significantly only on the repulsive wall. While performing the calculations, we ran into some computational difficulties when trying to converge the RCCSD(T) calculations for the  $^2\Pi$  state at  $R > 2.0 \text{ \AA}$ , prior to performing the

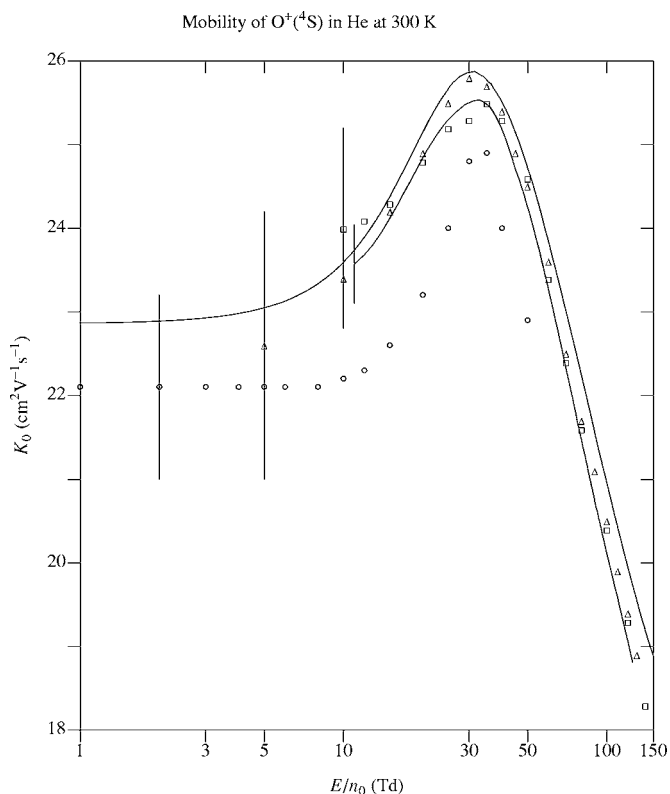


FIG. 2. Standard mobility of O<sup>+</sup>(<sup>4</sup>S) ions in He gas at 300 K, as functions of  $E/n_0$ . The lower curve represents the present, smoothed experimental values, as given by Eqs. (2) and (3). The upper curve represents the values computed from the present *ab initio* potentials obtained by combining the spin-orbit <sup>4</sup> $\Sigma^-$  curve below 2 Å with the RCCSD(T) curve at larger separations. The experimental values, with representative error bars, are from Lindinger and Albritton (Refs. 7 and 37) (triangles), Johnsen *et al.* (Refs. 10 and 39) (squares), and Viggiano *et al.* (Refs. 11 and 39) (circles).

spin-orbit calculations. We quickly noticed, however, that the effect of the spin-orbit interaction in this region was essentially negligible, and so we combined the spin-orbit <sup>4</sup> $\Sigma^-$  curve below 2 Å with the RCCSD(T) curve thereafter. The spline-fitted curve did not show any discontinuity at the join.

Our RCCSD(T) potential had a well depth of 1.458 mhartree at an ion-neutral separation of 4.475 bohr. These are in good agreement with the results obtained by Simpson *et al.*,<sup>9</sup> 1.42 mhartree at 4.57 bohr, and by Frenking *et al.*,<sup>13</sup> 1.27 mhartree at 4.67 bohr. Hogreve<sup>17</sup> did not report parameters for the <sup>4</sup> $\Sigma^-$  state, but found a well depth of 18 mhartree at 2.28 bohr for the <sup>2</sup> $\Pi$  state, while our calculations gave 17.86 mhartree at 2.253 bohr.

We find there are seven bound levels for the <sup>4</sup> $\Sigma^-$  ground state of HeO<sup>+</sup>. Relative to the minimum at  $-320.063$  cm<sup>-1</sup>, the ground ( $v=0$ ) state is at  $72.6$  cm<sup>-1</sup>, and the  $v=1$  level at  $112.1$  cm<sup>-1</sup>. Relative to the asymptote, the  $v=0-6$  levels are at  $-247.5108$ ,  $-135.4159$ ,  $-63.9567$ ,  $-24.9033$ ,  $-7.2601$ ,  $-1.2706$ , and  $-0.1267$  cm<sup>-1</sup>.

The presence of spin-orbit coupling dramatically affects the shape of the <sup>2</sup> $\Pi$  state close to the minimum, and so will have severe consequences for its spectroscopy. Consequently, we did not investigate the bound levels for the <sup>2</sup> $\Pi$  state.

To further test our *ab initio* potential, it was used in tabular form as input to a modified version of the program

TABLE II. Statistical comparison of experimental mobilities (accuracy of 2.5%) and calculated values (precision of 0.1%).

Data	$T$ (K)	$E/n_0$ (Td)	Accuracy (%)	Precision (%)	$N$	$\delta$	$\chi$
43	4.35	2–23	2	0.2	15	-1.44	1.69
		23–33	2	2	5	-0.16	0.38
		33–42	2	0.2	8	0.03	0.20
11	93	1–15	5	0.2	10	3.04	3.05
1	293	10–140	5	0.2	15	-0.28	0.43
11	298	1–50	5	0.2	16	-0.98	1.03
7	300	5–130	7	0.1	18	-0.21	0.24
Present	300	11–27	2.5	0.1	16	-0.45	0.46
		27–42	2.5	0.1	15	-0.50	0.50
		42–125	2.5	0.1	83	-1.27	1.32
11	568	1–50	5	0.2	16	-1.20	1.21

QVALUES (Refs. 34 and 35) to calculate transport cross sections with a numerical precision of 0.015% between  $10^{-7}$  and 1 hartree. The cross sections were then used in program GRAMCHAR (Ref. 36) to calculate the transport coefficients with a numerical precision of 0.1% for the ion mobility and 1% for the ion diffusion coefficients parallel and perpendicular to an electrostatic field. The results have been entered into the gaseous ion transport database<sup>29</sup> maintained at Chatham College.<sup>30</sup>

Figure 2 compares the experimental and theoretical results of the present work to the experimental values obtained by others. The good agreement warrants a statistical comparison of the present and previous experimental results<sup>38,39</sup> against values calculated from the present interaction potential. This comparison is given in Table II, where negative values for  $\delta$  indicate that the experimental values lie below the calculated ones (see Fig. 2). For the present data, the difference becomes statistically significant ( $|\delta| > 1$ ) only above 42 Td, and even here they are only marginally significant. The fact that  $\chi$  is only slightly larger than  $|\delta|$  indicates that the difference is nearly the same in all regions of  $E/n_0$  shown on Fig. 2. More information about  $\delta$  and  $\chi$  is given elsewhere.<sup>40</sup>

The statistical comparison in Table II supports the previous finding<sup>11</sup> that the experimental values at 93 K are inconsistent with the other data and should be ignored. The data at 4.35 K (Ref. 41) are in good agreement with the calculations above 23 Td, but the values at low  $E/n_0$  are below the calculated values by an amount that is statistically significant. It is noteworthy that essentially all of the trustworthy experimental values lie below the calculated values, indicating that the present potential may still have room for improvement.

## V. CONCLUSIONS

New experimental measurements are reported for the mobility of O<sup>+</sup> ions in He gas at 300 K. These data have been obtained in a way that avoid the injection effects that can produce large uncertainties. By injecting He<sup>+</sup> ions into a mixture of helium with less than 0.01% O<sub>2</sub>, reaction (1) produced sufficient O<sup>+</sup> ions in the <sup>4</sup>S state to allow the mobility to be determined with an accuracy of 2.5%.

The new values for the mobility of  $O^+$  ions in He are in good agreement with previous data, which generally has a claimed accuracy of only 5%. The accuracy of our new values allows them to serve as a stringent test of a new *ab initio* potential that we have calculated using the RCCSD(T) method employing the aug-cc-pV5Z basis set with counterpoise corrections. The present experimental values lie below the calculated ones, but the difference becomes statistically significant only at moderate and high values of the ratio of the electric field strength to the gas number density, and even there they are only marginally significant.

The present potential is the best one presently available for the  $4\Sigma^-$  state of  $HeO^+$ . Based on the statistical comparisons in Table I, however, it seems possible that there is still room for improvement of this potential.

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