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We present a systematic investigation of the accuracy of the various theories and basis sets that can be applied to study the interaction of Cl⁻ ions with Ar atoms. It is conclusively shown that gaseous ion mobility can distinguish among theoretical ion-neutral interaction potentials. Based on the conclusions, high-level *ab initio* potential energy curves are obtained for all of the Cl⁻–RG (RG = He–Rn) complexes. Spectroscopic constants have been derived from these potentials and are compared to a range of theoretical and experimental data, to which they generally show good agreement. General trends are discussed in comparison to other halogen-rare gas complexes previously studied. The potentials also have been tested by using them to calculate transport coefficients for Cl⁻ moving through a bath of RG atoms. © *2011 American Institute of Physics*. [doi:10.1063/1.3598472]

I. INTRODUCTION

The interaction of halide ions with gaseous atoms or molecules is of considerable applied interest, e.g., in the study of plasmas, gas discharges, and photodissociation in regions of the upper atmosphere. A clear understanding of such experiments requires accurate knowledge of the potential energy functions that govern the interactions, and a good starting point for acquiring such knowledge is for halide ions interacting with the rare gases. Here, both of the colliding particles have closed shells, so only a single ground state interaction potential will be involved and it will depend only upon the internuclear separation, R. Some of us have previously published high-level *ab initio* curves for the rare gas (RG) atoms interacting with F⁻,[1] Br⁻,[2,3] and I⁻.[4] We now extend this to the corresponding complexes involving Cl⁻, for which a considerable amount of transport data is available[5–13] but only limited scattering[14,15] and spectroscopic data.[16–20]

In 1981, mobility and diffusion data[9,10] for Cl⁻ ions in Xe were used[21] to test the well depth of the potential that had been inferred from differential scattering cross sections.[14] The transport data suggested a lower bound of 0.11 eV, while the scattering data gave an upper limit of 0.14 eV; both were consistent with the value of 0.135 eV found[13] by direct inversion[23] of the mobility data, but were substantially smaller than the earlier estimate by Riveros *et al.*[22]

Also in 1981, Viehland *et al.*[24] used existing mobility and diffusion data[7–10] for Cl⁻ ions in Ar to check the accuracy of a Hartree-Fock potential[25] for the system and of a potential inferred from scattering measurements with ion beams.[15] The theoretical calculations were in good agreement with the transport data for values of E/n_0, the ratio of the electrostatic field strength to the gas number density, above 200 Td (1 Td = 10^{-21} Vm²), but they were in significant disagreement at lower values. It was concluded that the potentials give a poor account of the well and long-range attraction, but that they give a reasonable account of the repulsive wall of the interaction. Similar conclusions were reached in 1984 for Cl⁻ interacting with the other rare gases.[26,27]

Success in obtaining the well depth of Cl⁻–Xe by direct inversion of the mobility data led Kirkpatrick and Viehland[28] to consider similar determinations for all of the halide ions in the rare gases. Their directly determined potentials covered a wide range of R, since they made use of data covering wide ranges of E/n_0. The potentials were the most accurate ones available at the time, from any source; in favorable cases, they were expected to be accurate within 10% at all R. Their accuracy led to the development of a universal scaling scheme for closed-shell interactions;[29] for many years these Koutselos-Mason-Viehland (KMV) model potentials represented the best information available about such ion-neutral interactions. A rival functional potential was the extended Tang-Toennies (ETT) potential.[30–32]

By 1995, *ab initio* calculations of atomic ion-atom interaction potentials finally began to become accurate enough to predict transport, scattering and spectroscopic data that agreed with the measured values within the mutual uncertainties. A test in 1996 (Ref. 33) established that Cl⁻–RG many-body perturbation theory (MBPT) calculations[34,35] were as accurate as the directly determined potentials and the potentials obtained by further extension of the ETT functional form,[36] and that they were more accurate than the KMV and original ETT models.

Highly accurate, *ab initio* coupled cluster calculations with single, double, and non-iterative triple excitations,

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CCSD(T), using extended basis sets augmented by bond functions, were performed for Cl^- interacting with Ar and Kr in 2001.[37] Analytical fits to the *ab initio* points were shown to be capable of reproducing all of the available experimental transport data as well as the results of zero electron kinetic energy (ZEKE) spectroscopy.[19] Hence model potentials are declining in use as representations of ion-neutral interaction potentials.

There has been considerable theoretical work recently on Cl^-–RG interaction potential energy curves at the CCSD(T) level. Bera and Das[38] studied RG = He–Kr employing aug-cc-pVTZ basis sets, while Naumkin and McCourt[39] employed aug-cc-pVQZ basis sets for RG = He–Ar. Cl^-–Ar has also been studied by Irikura[40] using aug-cc-pV(T+d)Z and by Sun *et al.*[43] using aug-cc-pVQZ basis sets.

Experimental work has continued apace. In addition to those already mentioned, mobility measurements have been made by Dotan *et al.*[44] and by Viggiano *et al.*[45] Diffusion coefficients have been obtained by Eisele *et al.*[11] Cross sections and transport properties for Cl^-–RG (RG = He–Xe) have been presented by Petrović *et al.*[46] using momentum transfer theory and Monte Carlo simulations. Experimental ZEKE spectra have been obtained for Cl^-–RG (RG = Ar–Xe) by Neumark's group[16,17,20] and for Cl^-–Ar by Distelrath and Boesl.[18]

To our knowledge, there has been no previous *ab initio* work on Cl^-–RG complexes involving Xe or Rn, no transport measurements involving Rn, and no spectroscopy involving He, Ne, or Rn.

In Sec. II we describe the methods used to compute the Cl^-–RG potential energies, the mobility values, and the spectroscopic parameters. In Sec. III, we examine the capabilities of a range of *ab initio* approaches for the calculation of an accurate Cl^-–Ar potential energy curve, and we demonstrate that very high-level calculations are required to generate potentials that are able to produce results that are in good agreement with experimental data. Accordingly, in Sec. IV we report such potentials for each of the Cl^-–RG systems, RG = He–Rn. In Secs. V and VI, we test our most accurate potentials by comparing transport data calculated from them with the available experimental data. General conclusions are given in Sec. VII.

II. COMPUTATIONAL METHODS

Binding energies at different internuclear separations, R, for Cl^-–Ar were computed at the HF, MP2, MP4, QCISD(T), and CCSD(T) levels of theory employing different standard, relatively small, basis sets using GAUSSIAN03,[47] making corrections for basis set superposition error (BSSE) on a point-by-point basis using the full counterpoise methods of Boys and Bernardi.[48] In addition, higher level CCSD(T) potential energy curves for the Cl^-–RG species were computed using MOLPRO[49] employing large aug-cc-pVXZ type basis sets that were augmented with extra basis sets of diffuse functions. The details of these CCSD(T) calculations are described as follows.

For RG = He–Ne, we have employed standard aug-cc-pV5Z and aug-cc-pV6Z basis sets[50–52] while for Ar we em-

ployed aug-cc-pV(5+d)Z and aug-cc-pV(6+d)Z basis sets;[53] in all three cases, we extended these by one further diffuse function of each angular momentum type, obtained by an even-tempered extrapolation of the most diffuse functions in the standard basis set. For RG = Kr–Rn, we employed the ECP10MDF, ECP28MDF, and ECP60MDF effective core potentials,[54] together with aug-cc-pVQZ and aug-cc-pV5Z valence basis sets,[54] again augmented by extra sets of diffuse functions. In each case, the corresponding aug-cc-pV(X+d)Z basis sets[53,54] were used for chlorine. Each potential energy curve was calculated for about 50 values covering a wide range of R, from about 2.8 to 95 bohr. Each point was corrected for BSSE using the full counterpoise correction. For RG = He–Ar, the interaction energies obtained using the quintuple-ζ and sextuple-ζ basis sets were pointwise-extrapolated to the complete basis set (CBS) limit using the $1/X^3$ formula;[55,56] for RG = Kr, Xe, and Rn we extrapolated from quadruple-ζ and quintuple-ζ in the same way. In each case, the extrapolated curves were employed for the subsequent calculation of the spectroscopic and transport coefficients.

The reduced mobility, diffusion coefficients parallel and perpendicular to an electrostatic field, and other transport properties of Cl^- moving in trace amounts through the RG were determined in a two-step procedure. The first step was to use the potential energy values to compute the transport cross sections as functions of the collision energy, using program QVALUES.[57,58] An improved version of this program became available[58] after the present calculations were started, but we did not use it in order to remain consistent with the Cl^-–Ar calculations in Sec. III of this paper. It should be noted that calculations with the new program indicated that it is not necessary to redo results obtained with QVALUES as long as they converged to the requested accuracy (here, 0.1% or better). In addition, in some cases it was necessary to apply small corrections to the computed potentials in order to force them to merge smoothly at large values of R into the ion-induced dipole potential[59] that is known to be asymptotically correct.

In the second step, the transport cross sections were used in the program GC (Refs. 60 and 61) to determine the transport coefficients of both $^{35}Cl^-$ and $^{37}Cl^-$ as functions of E/n_0 at the temperatures used in the experiments against which our results were to be compared in the naturally occurring isotopic mixtures of the RG. The numerous results have been placed in the database that was maintained at Chatham University but is now available at www.icecat.laplace.univ-tlse.fr. The calculated mobilities are generally precise within 0.1%, which means that the numerical techniques in QVALUES and GC have converged within 0.1%. The calculated diffusion coefficients are generally precise within 0.5%. Although there are regions of E/n_0 for which the calculations are less precise than this, in all cases the calculations are more precise than the accuracy claimed for the experimental values. This assumes, of course, that the present potentials are correct.

The accuracy of the computed potentials was assessed by evaluating four parameters: PTS, RMS, δ, and χ. The experimental and computed mobility values were determined at 100 evenly spaced E/n_0 values spanning the range of experimental data. PTS is the number of evenly spaced computed

mobility values falling within the limits of experimental error across the entire range of E/n_0 values (out of 100); since the maximum value occurs when PTS = 100, this can be interpreted as a percentage. RMS is the root mean square of the difference between the experimental and computed mobility values across the 100 E/n_0 values. Here, δ and χ were previously defined[62] as the ratio of the average percentage difference to the maximum combined percentage error expected, and the ratio of the standard deviation of the percentage differences to the root mean square of the maximum combined percentage deviation expected, respectively. In general, we can state that accurate potentials are those for which the computed mobility values have PTS close to 100, and RMS, δ, and χ values close to zero.

The LEVEL program[64] was employed to calculate rovibrational energy levels for each potential energy curve. From these, the lowest three vibrational levels (rovibrational levels having J = 0) were calculated and were least-squares fitted to standard Morse expressions to obtain the spectroscopic parameters. The force constants, k, have been calculated using the simple harmonic relationship. The most abundant naturally occurring isotope of each element was used in all cases (^{35}Cl, ^{4}He, ^{20}Ne, ^{40}Ar, ^{84}Kr, ^{132}Xe, and ^{222}Rn).

III. Cl⁻–Ar

Because so much previous work has been devoted to Cl⁻–Ar, this system is ideal for investigating how basis sets and correlation methods impact the accuracy of the interaction potential when assessed by using it as the input for computing the reduced mobility of Cl⁻ in argon across the entire range of experimentally reported E/n_0 values. Figure 1 demonstrates the impact of basis set selection on the computed mobility val-

ues. The basis set 6-311++G(3df,3pd) does not yield transport data within the range of experimental error, but the aug-cc-pVζZ (ζ = Q, 5, 6, ∞) series of basis sets converge to the actual data points upon reaching the CBS limit. This observation suggests that the uncertainties in the experimental data[7–10] are smaller than those originally reported. All of the tested basis sets were able to predict mobility values within the limits of experimental error at high E/n_0 values, but they predict substantially different mobility values at intermediate and low E/n_0 values. Since mobilities at low and high E/n_0 values are associated with the long- and short-range potential values, respectively, we can conclude that most basis sets are adequate for predicting short-range repulsive interactions, but larger basis sets (quadruple-ζ or larger) are required for accurate potential energy calculations at large ion-neutral separations. Table I reports the characteristic features for each of the computed potentials.

Using the aug-cc-pV5Z basis set we tested potentials generated using several electron correlation methods. As shown in Fig. 2, both perturbation (MP4 and MP2) and coupled-cluster (CCSD(T)) methods generated potentials that yielded mobility values within the limits of experimental error across the entire range of E/n_0 values. The high computational cost of MP4 and CCSD(T) methods limits their use in calculations on larger molecular systems, and the accuracy of the faster MP2 method offers the possibility for its use in these cases.

IV. NEW Cl⁻–RG POTENTIAL ENERGY CURVES

Based on the outcomes of the Cl⁻–Ar work, and in line with our previous work on a range of species,[61, 65–73]

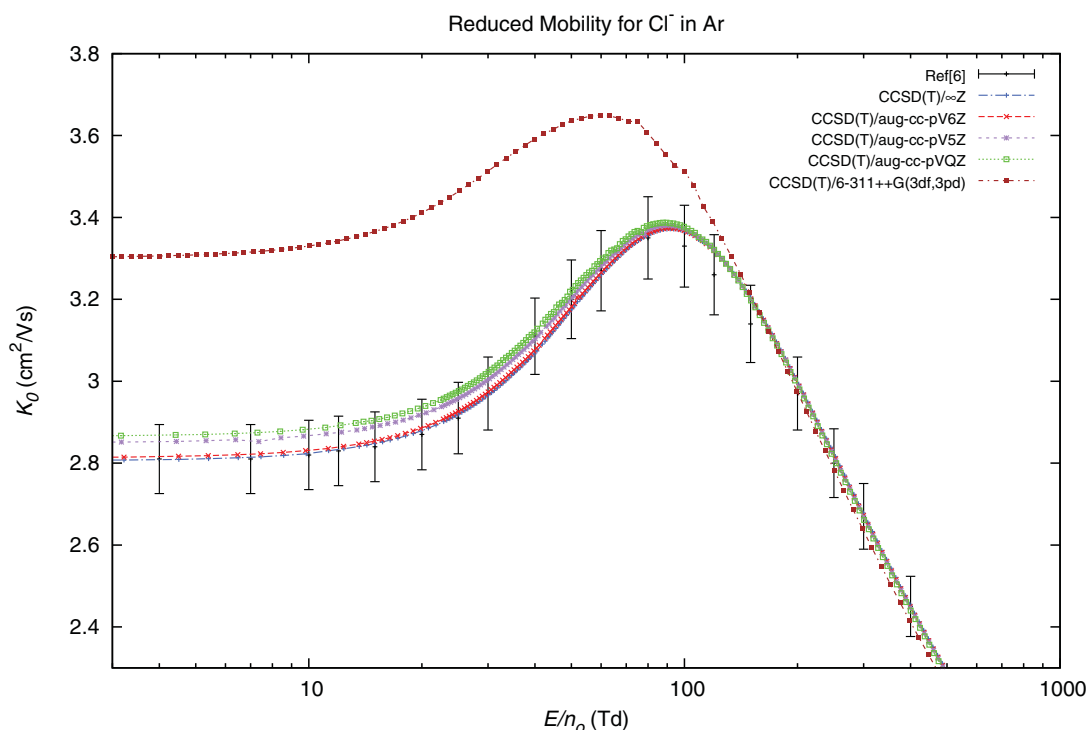FIG. 1. Comparison of experimental (Ref. 6) and computed reduced mobility values for Cl⁻ in Ar at 297 K with selected basis sets and constant correlation method. All values are corrected for BSSE on a point-by-point basis.
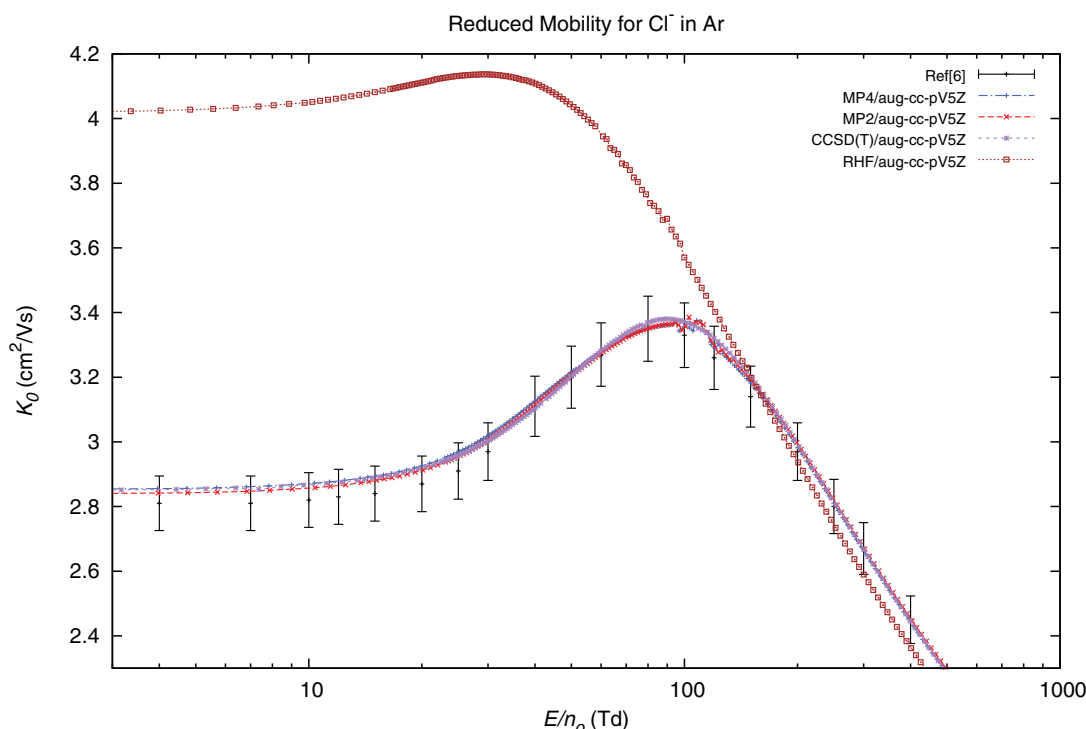
FIG. 2. Comparison of experimental (Ref. 6) and computed reduced mobility values for Cl^- in Ar at 297 K with selected correlation methods and constant basis set. All values are corrected for BSSE on a point-by-point basis.

including anionic species,[1–4] we calculated CCSD(T) potential energy curves, extrapolated to the basis set limit, for all of the Cl^-–RG species as described in Sec. II. From these, spectroscopic and mobility data were calculated and subsequently compared to experimental data. Figure 3 shows the potentials in the region of their minima. A complete listing of the tabulated potential values is given as supplementary material[63] The spectroscopic constants derived from the LEVEL program[64] for Cl^-–RG are given in Table II.

Neumark's group have derived R_e and D_e values from potentials which had been fitted to ZEKE spectra.[16] They obtained R_e and D_e values of 3.71 $\pm$ 0.08 Å and 523 $\pm$ 5 cm^{-1} for Cl^-–Ar. Distelrath and Boesl[18] have also studied Cl^-–Ar using ZEKE spectroscopy, and they used two different methods to calculate D_e. The first was a Birge-Sponer analysis that gave the rather low result of 350 cm^{-1}. The second method used the measured electron affinities together with the Birge-Sponer extrapolated

TABLE I. Properties of the $^{35}Cl^-$–Ar potentials at 300 K. Column 1 lists the method/basis set employed for the potential energy calculation. PTS, RMS, δ, and χ are measures of agreement between the calculated and experimental mobility values, as defined in Sec. II of the text. Section II also gives a detailed description of the basis sets employed in the CCSD(T) calculations. D_e is the well depth (millihartree), R_e is the separation at the potential minimum (Angstrom), and σ_0 is the separation (Angstrom) at which the potential energy changes sign.

Method/basis set	PTS	RMS	δ	χ	D_e	R_e	σ_0
CCSD(T)/∞Z	100	0.0150	−0.05	0.15	2.35	3.67	3.14
MP4/aug-cc-pV6Z	100	0.0214	−0.10	0.23	2.33	3.67	3.14
CCSD(T)/aug-cc-pV6Z	100	0.0241	−0.12	0.24	2.32	3.68	3.14
MP2/aug-cc-pV6Z	100	0.0252	−0.17	0.27	2.37	3.66	3.15
MP4/aug-cc-pV5Z	100	0.0258	−0.14	0.28	2.29	3.68	3.15
MP2/aug-cc-pV5Z	100	0.0277	−0.22	0.30	2.33	3.66	3.13
CCSD(T)/aug-cc-pV5Z	100	0.0372	−0.30	0.37	2.30	3.68	3.15
CCSD(T)/aug-cc-pVQZ	100	0.0461	−0.40	0.48	2.26	3.70	3.16
MP2/6-311++G(3df,3pd)	80	0.186	−0.92	1.81	1.75	3.79	3.26
QCISD(T)/6-311++G(3df,3pd)	79	0.212	−0.92	2.04	1.64	3.83	3.29
CCSD(T)/6-311++G(3df,3pd)	77	0.213	−0.93	2.04	1.64	3.84	3.30
MP4/6-311++G(3df,3pd)	78	0.214	−0.95	2.05	1.64	3.83	3.29
QCISD/6-311+G(3df,3pd)	75	0.253	−1.07	2.37	1.52	3.87	3.32
CCSD/6-311++G(3df,3pd)	75	0.255	−1.07	2.38	1.52	3.87	3.33
MP4/aug-cc-pVDZ	75	0.306	−1.17	2.78	1.37	3.91	3.36
RHF/aug-cc-pV5Z	74	0.443	−1.35	3.69	0.95	4.15	3.55
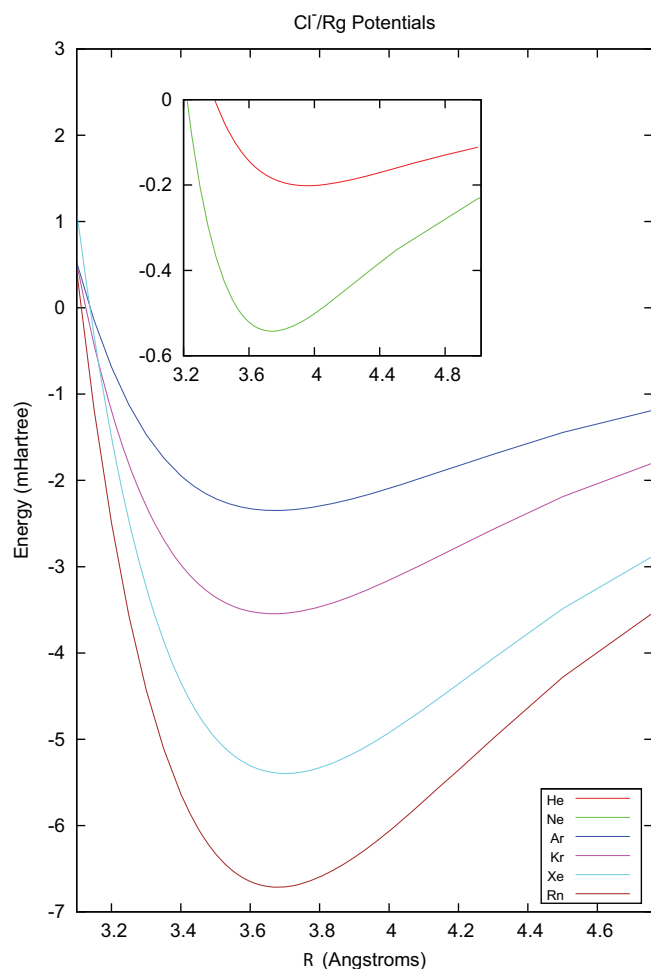
FIG. 3. Interaction potentials for Cl⁻ in the rare gases in region of minima.

TABLE II. Characteristic features and spectroscopic constants for F⁻–RG, Cl⁻–RG, and Br⁻–RG. All values were calculated at the RCCSD(T) level for the most abundant naturally occurring isotopes. Here, R_e is the equilibrium bond length in Å, D_e is the depth of the potential in cm⁻¹, D_0 is the energy difference in cm⁻¹ between the zero-point and the asymptote, ω_e is the harmonic vibrational frequency in cm⁻¹, $\omega_e x_e$ is the anharmonicity constant in cm⁻¹, B_e is the equilibrium rotational constant in cm⁻¹ at the minimum, and k is the harmonic force constant in Nm⁻¹.

	R_e	D_e	D_0	ω_e	$\omega_e x_e$	B_e	k
F⁻–He	3.26	74.5	52.5	41.6	6.13	0.426	0.34
F⁻–Ne	3.14	188.1	164.5	48.8	3.64	0.168	1.79
F⁻–Ar	3.02	879.2	833.4	92.7	2.94	0.141	9.46
F⁻–Kr	2.99	1366.7	1315.2	103.8	2.37	0.120	15.70
F⁻–Xe	2.96	2230.2	2168.7	123.2	2.06	0.115	24.77
F⁻–Rn	2.94	2805.8	2739.0	134.8	1.90	0.111	32.40
Cl⁻–He	3.96	44.2	29.3	26.3	4.18	0.298	0.15
Cl⁻–Ne	3.74	119.1	103.7	31.4	2.37	0.095	0.74
Cl⁻–Ar	3.67	515.4	488.8	54.0	1.68	0.067	3.21
Cl⁻–Kr	3.72	778.1	749.8	57.1	1.25	0.051	4.75
Cl⁻–Xe	3.70	1184.4	1152.5	64.3	1.03	0.045	6.74
Cl⁻–Rn	3.68	1473.7	1439.9	68.1	0.92	0.041	8.27
Br⁻–He	4.24	35.5	23.2	24.7	4.62	0.216	0.14
Br⁻–Ne	3.97	100.6	88.4	25.0	1.83	0.064	0.59
Br⁻–Ar	3.91	431.6	411.8	40.1	112	0.041	2.53
Br⁻–Kr	3.91	650.0	630.5	39.2	0.71	0.027	3.71
Br⁻–Xe	3.95	975.9	954.9	42.2	0.54	0.022	5.23
Br⁻–Rn	3.92	1216.4	1194.9	43.1	0.45	0.019	6.44

D_0 value of the neutral Cl⁻–Ar complex: this gave a larger value of 480 cm⁻¹. There have been a number of theoretical studies on the Cl⁻–Ar complex. Only *ab initio* studies at the CCSD(T) level are discussed here and below. These have employed aug-cc-pVTZ or aug-cc-pVQZ quality basis sets, and it is therefore not surprising that the calculated dissociation energies are close to, but typically somewhat below ours, which have used larger basis sets, and have been extrapolated to the basis set limit. Buchachenko *et al.*[37] used both aug-cc-pVTZ and aug-cc-pVQZ basis sets, each further augmented by a set of (3s3p2d) bond functions placed midway between the nuclei. Since the potentials they obtained were so similar, they only used the former basis set for Cl⁻–Kr (see below). In all of their calculations, the frozen-core approximation was used. The R_e value that they obtained was 3.69 Å for Ar, which is in good agreement with our value of 3.67 Å. Their D_e value of 500.6 cm⁻¹ is in satisfactory agreement with our value of 515.4 cm⁻¹, obtained from extrapolating larger basis sets. Naumkin and McCourt[39] have employed aug-cc-pVQZ level basis sets, and consequently their results are close to ours, with R_e = 3.71 Å and D_e = 476.7 cm⁻¹. Sun *et al.*[43] also employed aug-cc-pVQZ basis sets, with additional (3s3p2d1f) bond functions, but with the g functions removed from the basis set. They obtained a R_e value identical to ours, and D_e = 493.4 cm⁻¹. Irikura[40] has calculated the

potential curve for Cl⁻–Ar at the CCSD(T)/aug-cc-pV(T+d)Z level, obtaining R_e = 3.72 Å and D_e = 434.5 cm⁻¹; in addition, single-point energies employing up to sextuple-ζ basis sets were calculated at this R_e value and extrapolated to the basis set limit; these yielded an extrapolated CCSD(T) interaction energy of 514.9 cm⁻¹ which is almost identical to our value of 515.4 cm⁻¹. Very recently Bera and Das[38] have performed calculations on the interaction of He–Kr with Cl⁻ using aug-cc-pVTZ basis sets, and using the CCSD(T) method; the potential energies then appear to have been fitted to a Lennard-Jones potential[41] from which spectroscopic parameters were obtained. For Cl⁻–Ar, their value of R_e = 3.72 Å is close to the present value, and those of previous workers; their D_e value of 443.6 cm⁻¹ is in line with some of the previous values, but is significantly lower than the present value of 515.4 cm⁻¹. It is noteworthy that the theoretical D_e values that are most consistent with those derived from experimentally determined ZEKE spectra (523 ± 5 cm⁻¹) are from our work (515.4 cm⁻¹) and from Irikura (514.4 cm⁻¹),[40] clearly showing these species demand the highest levels of theory in order to obtain converged energy values. The R_e values of our work (3.67 Å) and Irikura (3.72 Å) are similar and within the range of experimental error reported from ZEKE spectroscopy (3.71 ± 0.08 Å).

Cl⁻–Kr has also been studied, albeit to a lesser extent than Cl⁻–Ar. Again, Neumark *et al.* have obtained R_e and D_e values from potential energy curves which have been fitted to experimental ZEKE results;[17] they report R_e = 3.83 Å and D_e = 772 ± 8 cm⁻¹. Buchachenko *et al.*[37] have also studied this complex using CCSD(T) calculations and employing an aug-cc-pVTZ+ *bf* basis set. The frozen-core approximation

was used; however, they also made one calculation in which all of the electrons were correlated except the $1s$ and $2s$ electrons of the chloride ion and the $1s$, $2s$, $2p$, and $3s$ electrons of Kr; this lowered the value of D_e by only 0.6%, so it was concluded that the frozen-core approximation is adequate. Their reported values are $R_e = 3.73$ Å and $D_e = 719.6$ cm^{-1}. Our calculated value of $R_e = 3.67$ Å is in good agreement with that of Buchachenko *et al.*, but a little lower than the ZEKE value. The recent CCSD(T)/aug-cc-pVTZ results from Bera and Das[38] yield a R_e value of 3.67 Å, which is in good agreement with our value of 3.72 Å, although it is noteworthy that their value is lower than their value for Cl$^-$–Ar; for D_e their value of 718 cm^{-1} is somewhat lower than our 778.1 cm^{-1} value, although it is in good agreement with Buchachenko *et al.*'s value. On the other hand, there is excellent agreement between the ZEKE value[17] for D_e and the present value of 778.1 cm^{-1}, again suggesting that these complexes are demanding from a computational point of view.

Neumark *et al.*[20] have also studied the Cl$^-$–Xe complex by ZEKE spectroscopy. The fitted potential yielded a R_e value of 3.57 ± 0.03 Å, which is significantly smaller than a CCSD(T) value of 3.80 Å from Schröder *et al.*,[42] which itself is in better agreement with the present value of 3.70 Å. The experimentally derived D_e value of 1176 ± 10 cm^{-1} is in good agreement with the present value of 1152.5 cm^{-1}, while the previous theoretical value from Schröder *et al.* of 980 cm^{-1} is significantly lower.

Bera and Das[38] have also reported CCSD(T)/aug-cc-pVTZ results for Cl$^-$–He and Cl$^-$–Ne. They obtained $R_e = 4.05$ Å for Cl$^-$–He, which is in fairly good agreement with our value; and $D_e = 24.2$ cm^{-1}, which is significantly below our value of 44.2 cm^{-1}. For Cl$^-$–Ne, they obtained $R_e = 3.72$ Å, which is in very good agreement with our value of 3.74 Å, but again poor agreement is seen between their D_e value of 88.7 cm^{-1} when compared to our value of 119.1 cm^{-1}.

Vibrational frequencies have also been reported for Cl$^-$–Ar, with the experimental fundamental ZEKE vibrational values of 53.1 cm^{-1} (Ref. 16) and 53.4 cm^{-1} (Ref. 18) being in excellent agreement with the present harmonic value of 54.0 cm^{-1}, and in good agreement with the calculated value of $\omega_e = 52.2$ cm^{-1} from Bera and Das.[38] No experimental anharmonicities have been reported; however, a calculated value of 2.73 cm^{-1} from Bera and Das is somewhat larger than the present value of 1.68 cm^{-1}, which could be attributable to their fitting of a wider range of the potential energy surface. Yourshaw *et al.*[16] also report an experimental ZEKE fundamental vibrational value of 55.5 cm^{-1} for Cl$^-$–Kr, which compares very well with the present harmonic value of 57.1 cm^{-1}, and the calculated harmonic value from Bera and Das of 55.1 cm^{-1}. Again there are no experimental anharmonicities, but our calculated value of 1.25 cm^{-1} is significantly lower than Bera and Das's value of 2.05 cm^{-1}. Finally, there has been an experimental fundamental vibration frequency of 41.43 cm^{-1} for Cl$^-$–Xe reported by Lenzer *et al.*,[20] which compares rather poorly with the present value of 64.3 cm^{-1}. We note that the present value is more in line with the increasing vibrational frequency as the RG atom gets heavier and more polarizable.

For completeness, we note that Bera and Das[38] also reported spectroscopic parameters obtained from fitted Lennard-Jones potentials for Cl$^-$–He and Cl$^-$–Ne. For Cl$^-$–He, they obtain $\omega_e = 29.9$ cm^{-1}, which is close to the present value of 26.3 cm^{-1}, while the anharmonic constant, $\omega_e x_e$, value of 12.00 cm^{-1} obtained by them is significantly larger than the present 4.18 cm^{-1} value; this is consistent with their use of a wider range of potential energy surface, where deviations from Morse behavior are likely to be large. A similar situation holds for Cl$^-$–Ne, where Bera and Das's ω_e value of 28.1 cm^{-1} is close to our value of 31.4 cm^{-1}, but their $\omega_e x_e$ value of 3.74 cm^{-1} is larger than our value of 2.37 cm^{-1}.

Rotational constants were also calculated by Bera and Das,[38] and in general, their B_e values are in good agreement with ours, although their value of $B_e = 0.48$ cm^{-1} for the Cl$^-$–He complex appears to be too high. To investigate this, we calculated B_e using their value of 4.05 Å for R_e, obtaining a value of $B_e = 0.286$ cm^{-1}, which is much closer to our value.

V. TRANSPORT PROPERTIES FOR Cl$^-$ IN He

We calculated the mobility, diffusion coefficients parallel and perpendicular to an electrostatic field, and other transport properties of Cl$^-$ moving in trace amounts through the RG as described in Sec. II. There are many sets of transport data for Cl$^-$ in He. Figure 4 shows a comparison of our calculated values at 300 K for ^{35}Cl$^-$ and ^{37}Cl$^-$ with the smoothed experimental values from 1976 (Ref. 6) and the raw values from 1979.[44] The agreement is excellent, with the calculated values being perhaps slightly below the experimental results at small E/n_0. An alternate and more compact way of comparing the experimental and theoretical values is with the statistical parameters described in previous work[62] and used in Tables I and III. The δ values in Table III for Cl$^-$ in He at 300 K are positive, indicating that the experimental values lie above the calculated ones. They are, however, much smaller than 1.0, indicating that the differences are not statistically significant. The χ values are not much larger than $|\delta|$, indicating that the differences are not strongly dependent upon E/n_0 and that there is not much scatter in the experimental data.

Table III shows that the smoothed experimental mobilities at 207 K and 299 K (Ref. 12) are slightly below the calculated values, while those at 297 K (Ref. 9) are, like those at 300 K, slightly above. None of the differences are statistically significant nor do they vary significantly with E/n_0. Moreover, the values of δ for ^{35}Cl$^-$ are so similar to those for ^{37}Cl$^-$ that our calculations cannot distinguish which of the isotopes was used in the experiments; based on relative abundance, it is likely that ^{35}Cl$^-$ was used.

Figure 5 shows the mobilities of ^{35}Cl$^-$ in He as functions of both E/n_0 and T. The well-known formula[59] for the polarization limit of the mobility gives $K_0 = 16.14$ cm^2/Vs, based on a helium polarizability of 0.20505 Å^3 and molar masses of 34.96885 and 4.00260 g/mol. This value applies only in the double limit where both E/n_0 and T are zero, so we see from Fig. 5 that even 4.35 K is not low enough for the mobility to equal the Langevin value.
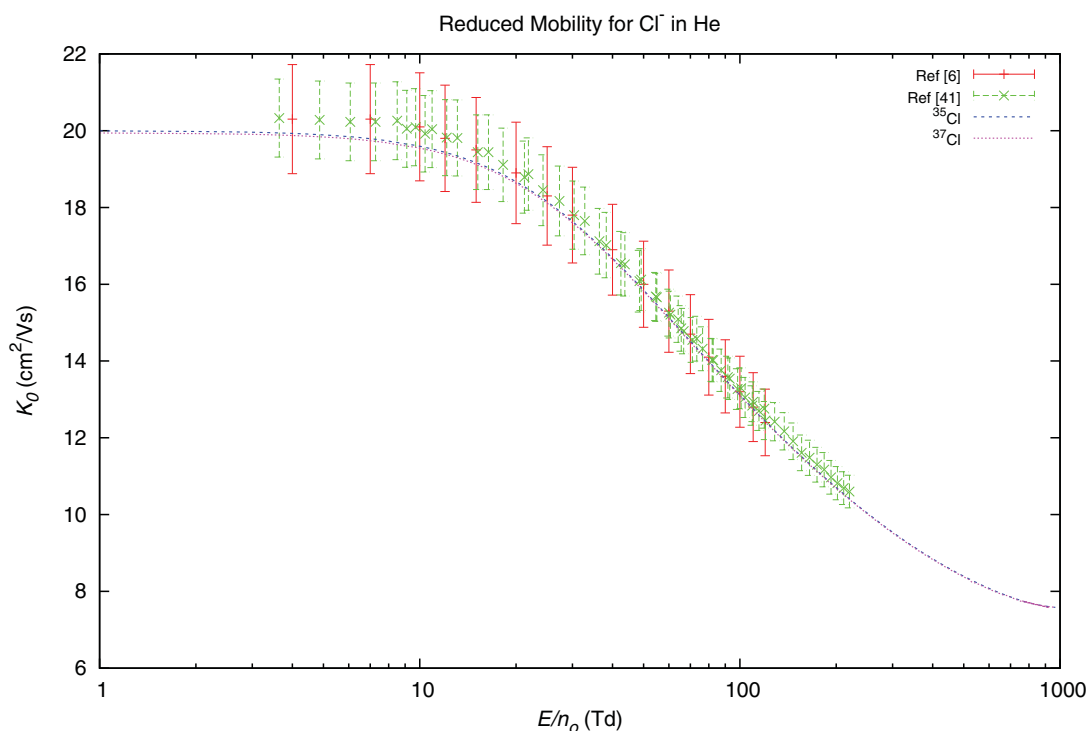
Reduced Mobility for Cl⁻ in He

FIG. 4. Comparison of experimental (Refs. 6 and 42) and computed reduced mobility values for isotopes ^{35}Cl and ^{37}Cl in He at 300 K.

The mobility maximum in Fig. 5 of 23.685 cm^2/Vs for 4.35 K occurs at $E/n_0 = 15.40$ Td. Using these values in the Wannier formula[59] gives a collision energy of 3.35 $\times 10^{-4}$ hartree. As expected, this is comparable to the well depth of the potential, 2.01×10^{-4} hartree. Also as expected, the mobility maximum disappears as the gas temperature increases.

The mobilities at very low E/n_0 are nearly constant at each gas temperature. This is because the electric field is so low that it has little influence on the average kinetic energy of the ions, compared to their thermal energy. We note, however, that the constant value changes substantially as the gas temperature increases. In addition, there is a slight decrease in the mobility at 4.35 K as E/n_0 increases below 5 Td, leading to
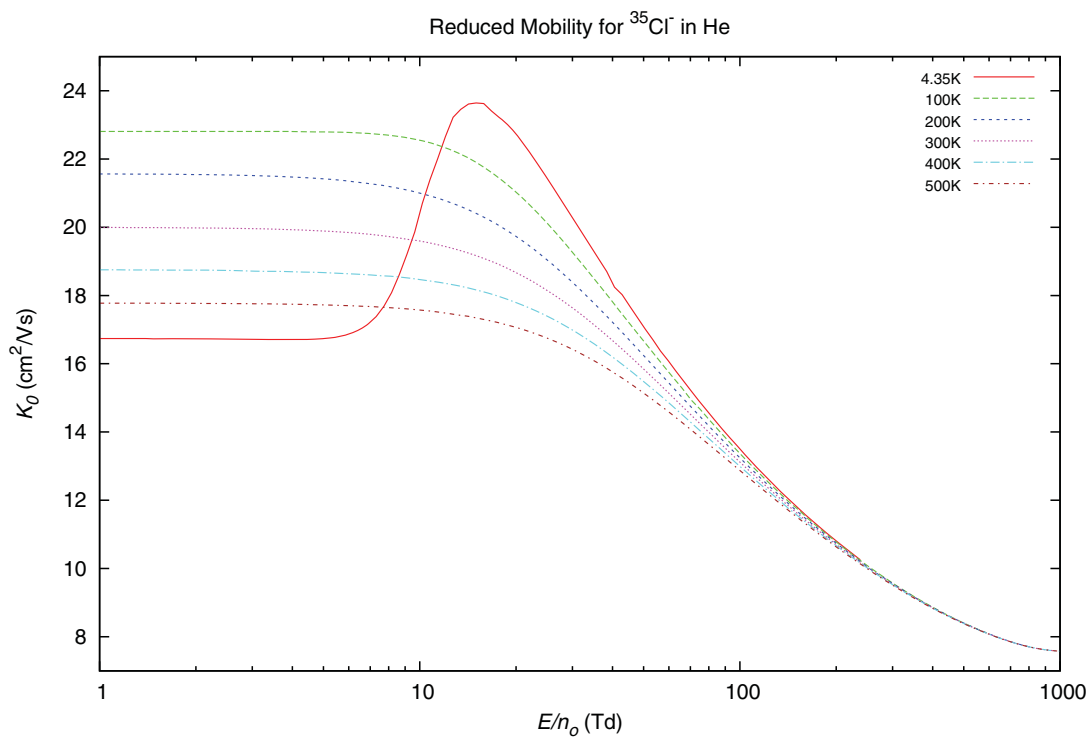
Reduced Mobility for ^{35}Cl⁻ in He

FIG. 5. Reduced mobility of ^{35}Cl⁻ in He as functions of field strength and temperature.

TABLE III. Statistical comparison of theoretical and experimental transport properties for Cl^- ions in RG. The properties listed are the reduced mobility (K_0), the product of the gas number density and the ion diffusion coefficient along the direction of the electric field ($n_0 D_L$), and the gas temperature (T, Kelvin). Range gives the range of E/n_0 in Td, N is the number of experimental data points in range, %E and %C, are the estimated maximum errors in the experiments and in the present calculations, respectively, and δ and χ are the statistical quantities described in Sec. II and earlier work.[62] The first pair of statistical quantities are for $^{35}Cl^-$ and the last for $^{37}Cl^-$.

RG	Properties	T	Reference	Range	N	%E	%C	δ	χ	δ	χ
He	K_0	207	12	4-10	5	5.0	0.1	−0.37	0.37	−0.32	0.32
		297	9	2-50	5	5.0	0.1	0.33	0.34	0.37	0.38
				50-153	5	4.0	0.1	0.19	0.21	0.24	0.25
				153-220	4	4.0	0.5	0.22	0.25	0.26	0.29
		299	12	3-15	8	5.0	0.1	−0.52	0.53	−0.47	0.48
		300	6	4-120	17	7.0	0.1	0.17	0.20	0.20	0.22
		300	44	3.6-50	26	5.0	0.1	0.33	0.35	0.37	0.40
				50-154	26	4.0	0.1	0.27	0.29	0.31	0.33
				154-220	8	4.0	0.5	0.32	0.32	0.37	0.37
Ne	K_0	300	10	2-69	26	2.0	0.1	0.36	0.73	0.79	1.00
				69-210	9	2.0	0.1	0.33	0.71	0.52	0.74
				210-405	5	2.0	0.1	0.95	1.18	0.88	1.01
			6	2-69	13	2.0	0.1	1.23	3.28	0.59	0.71
				69-210	5	2.0	0.1	−0.58	0.92	0.50	0.61
				210-400	3	2.0	0.1	0.52	0.55	0.76	0.78
	$n_0 D_L$	300	9	2-10	7	8.0	1.0	−0.40	0.53	−0.28	0.46
				10-69	8	12	1.0	0.50	0.51	0.59	0.59
				69-210	5	16	1.0	0.51	0.51	0.42	0.42
				210-400	3	20	1.0	0.38	0.38	0.27	0.27
Ar	K_0	297	8	2-65	26	2.0	0.1	−0.48	1.45	0.29	1.41
				65-210	28	2.0	0.5	−0.63	0.78	−0.14	0.50
				210-440	13	2.0	1.0	0.55	1.43	0.85	1.59
		300	9	4-48	9	3.0	0.1	−0.11	0.18	0.60	0.65
				48-210	7	3.0	0.5	−0.02	0.14	0.53	0.60
				210-400	3	3.0	0.5	0.04	0.07	0.34	0.35
		300	10	6-48	25	3.0	0.1	−0.19	0.80	0.33	0.87
				48-210	28	3.0	0.5	−0.32	0.59	0.06	0.50
				210-347	9	3.0	0.5	0.06	0.48	0.26	0.43
	$n_0 D_L$	300	9	5-15	6	8.0	1.0	0.98	1.29	1.20	1.47
				15-65	6	12	1.0	1.96	2.04	2.24	2.31
				65-210	5	16	8.0	0.62	0.66	0.73	0.75
				210-300	2	20	8.0	0.50	0.51	0.47	0.47
		300	75	6-65	30	5.0	1.0	3.76	5.15	3.86	5.28
				65-100	8	5.0	8.0	1.93	2.17	1.88	2.11
				100-347	24	10	8.0	0.92	1.17	0.99	1.26
Kr	K_0	300	9	4-37	9	2.0	0.1	−0.06	0.16	0.91	0.93
				37-106	5	2.0	0.5	0.47	0.50	1.44	1.44
				106-400	6	2.0	1.0	0.09	0.21	0.59	0.64
		300	10	3-37	23	2.0	0.1	0.23	0.81	1.21	1.45
				37-106	15	2.0	0.5	0.86	1.12	1.87	2.08
				106-411	20	2.0	1.0	0.24	0.60	0.78	0.97
	$n_0 D_L$	300	9	3-10	6	8.0	1.0	−0.16	0.25	0.06	0.21
				10-37	5	12	1.0	0.40	0.46	0.63	0.69
				37-106	5	16	8.0	0.30	0.44	0.49	0.60
				106-400	6	20	15	0.14	0.16	0.24	0.26
Xe	K_0	300	9	3-41	11	2.0	0.1	−0.10	0.30	0.97	1.02
				41-400	10	2.0	1.0	0.32	0.35	1.37	1.38
		300	13	3-41	18	2.0	0.1	−0.08	0.47	0.98	1.10
				41-460	31	2.0	0.1	0.39	0.53	1.54	1.63
	$n_0 D_L$	300	9	3-20	9	8.0	1.0	0.68	0.70	0.96	0.98
				20-41	3	12	1.0	0.44	0.44	0.73	0.73
				41-50	1	12	15	0.18	0.18	0.12	0.12
				50-150	5	16	15	0.26	0.36	0.61	0.74
				150-400	4	20	15	0.03	0.09	0.35	0.40

a mobility minimum; the reasons for this have been explained previously.[65]

The mobilities at high E/n_0 are almost independent of the gas temperature, since here thermal energies are small compared to the energies that the ions acquired from the electric field. Note from Fig. 5 that the high-field mobilities decrease steadily, but not quite as fast as the $(E/n_0)^{-1/2}$ behavior expected for rigid spheres. Hence, the ion-neutral interaction potential at small internuclear separations is strongly repulsive, but not infinitely steep.

Figure 6 shows how the zero-field reduced mobility, $K_0(0)$, for ^{35}Cl$^-$ ions in He varies with the gas temperature. The excellent agreement with the polarization limit (Langevin mobility) below 0.1 K indicates that the present interaction potential is highly accurate at large inter-nuclear separations. Another important point illustrated by Fig. 6 is that it shows a strong dependence of $K_0(0)$ upon gas temperature for T values from 300-500 K; such strong dependence is sometimes overlooked in ion mobility spectrometry (IMS) studies[74] in which the differences in zero-field mobilities are used to separate gas-phase ions. Another problem in IMS is recognizing how large E/n_0 can be before the reduced mobility varies from $K_0(0)$; an improved formula for estimating this upper limit was given in our previous work.[65]

VI. TRANSPORT RESULTS FOR Cl⁻ IN Ne–Rn

The δ values in Table III for Cl$^-$ in Ne at 300 K are small and positive when the raw data[10] are analyzed, indicating that the experimental values lie above the calculated ones, but that the differences are not statistically significant. However, when the smoothed values[6] are analyzed, the δ values exceed 1 at low E/n_0, are negative at intermediate E/n_0 and are positive at high E/n_0. The χ values are not much larger than $|\delta|$ for the raw data, indicating that the differences are not strongly dependent upon E/n_0 and that there is not much scatter in the experimental data. Again there is a big difference for the smoothed data,[6] where the χ values are much larger than $|\delta|$. This points to a previously unsuspected error in the smoothing of the experimental mobilities.

Figure 7 shows a comparison of our calculated values at 300 K for n_0D_L, the product of the gas number density and the diffusion coefficient along the field direction; values for both chloride isotopes are shown along with the smoothed experimental values from 1978.[9] The agreement is excellent, as can also be seen in the statistical results in Table III. The calculated values for ^{35}Cl$^-$ are in slightly better agreement with data than are those for ^{37}Cl$^-$, which is in accord with the statement by the experimenters that the ^{35}Cl$^-$ isotope was used.

Turning now to Ar, we see from the statistics in Tables I and III that the calculated mobilities are in excellent agreement with all of the available data, especially when the smoothed experimental mobilities[9] at 300 K are compared with the calculated values for ^{35}Cl$^-$. Apparently, the smoothing error made for Cl$^-$ in Ne was not repeated for the other RG. Note also that the differences in the δ values for the two isotopes are larger for Ar than for any of the other RG; this is due to the fact that the mobility primarily depends upon the ion mass through the inverse square root of the ion-neutral reduced mass, as illustrated more fully in a recent paper.[73]

The values of χ in Table III are substantially larger than $|\delta|$ when our calculated values of n_0D_L for Ar are compared to the raw experimental values.[75] This is because the experimental values are highly scattered, a problem that is largely
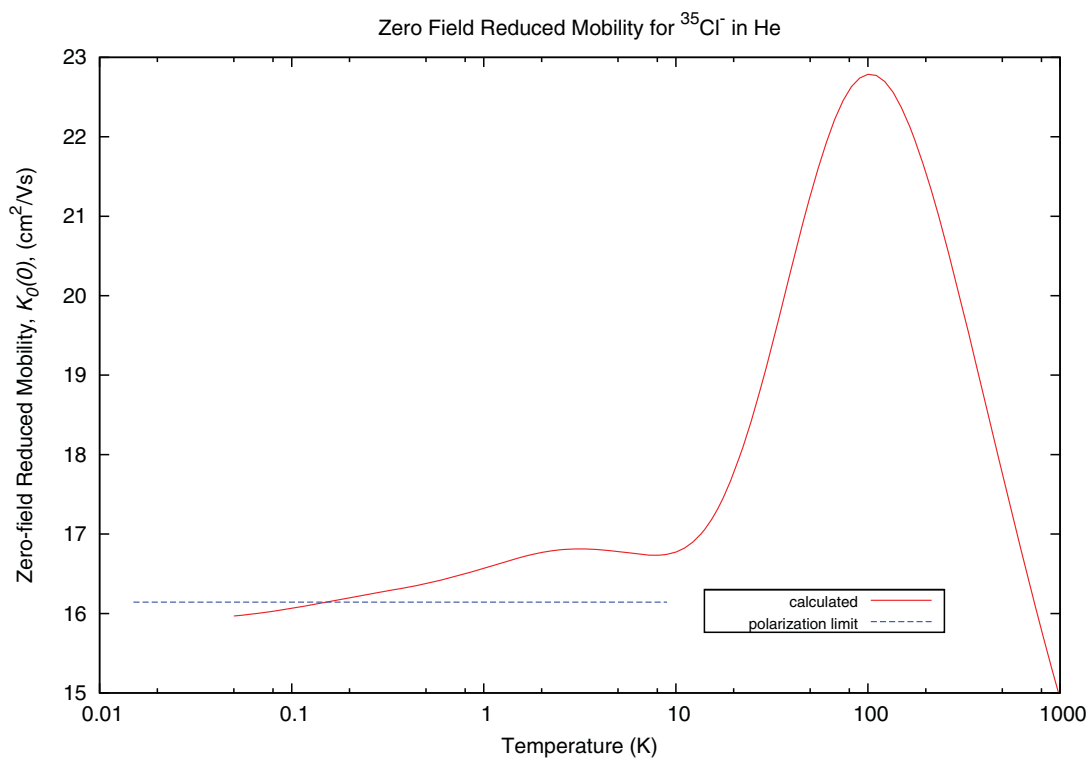

FIG. 6. Variation of zero-field reduced mobility for ^{35}Cl$^-$ in He with gas temperature. Horizontal line is the polarization limit (Langevin mobility).
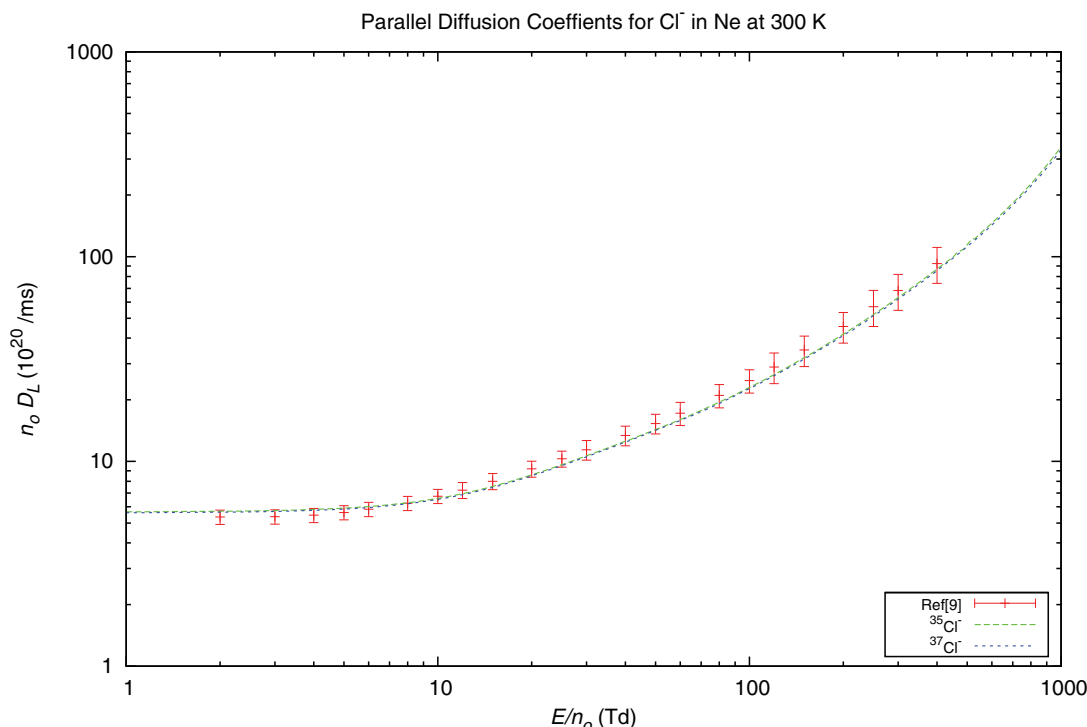
FIG. 7. Comparison of calculated and experimental (Ref. 9) products of the gas number density and the diffusion coefficient parallel to the field for Cl^- in Ne at 300 K.

solved by smoothing, which is why the χ values are not much greater than $|\delta|$ when our calculated values are compared to the smoothed values.[9] Nevertheless, there is a region of intermediate E/n_0 where even the smoothed data have a δ value substantially above one, even though the error estimates for the experimental values are relatively large. Until the experimental measurements are redone, the present theoretical values for the diffusion coefficients are likely to be the more reliable.

For Kr and Xe, the statistics in Table III indicate that there is excellent agreement between our calculated mobilities and the smoothed experimental values.[9] This is also the case for the smoothed values of $n_0 D_L$, although there are again rather large error bars on the experimental values. Finally, there are no transport data for Cl^- ions moving through Rn with which we can compare.

VII. CONCLUSIONS

We report the results of testing numerous potentials for the $Cl^- - Ar$ system. Potentials that accurately predict experimentally reported mobility values are those using quaduple-ζ or larger basis sets and perturbation (MP2, MP4) or coupled-cluster (CCSD(T)) correlation methods. The overall accuracies of our potentials are heavily dependent upon potential values at larger values of R where the $Cl^- - Ar$ interaction energy is very small and most susceptible to the quality of the correlation method and basis sets employed.

The trends observed in the $Cl^- - RG$ series are largely the same as the trends seen in the other halide ion-RG series. The CCSD(T) method has been shown to produce consis-

tently accurate potential curves in all of our halide ion-rare gas studies, as shown by the excellent agreement between experiments and our calculated gas transport values. Furthermore, these potentials have been employed to derive accurate spectroscopic constants. We have provided CCSD(T) potentials with complete basis set and pointwise BSSE corrections for each of the $Cl^- - RG$ systems. Excellent agreement between transport and/or spectroscopic data derived from these potentials and experimentally reported values, when available, has been demonstrated, leading us to conclude that the present potentials are the best currently available for these systems.

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