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Test of the interaction potentials of H^- and Br^- ions with He atoms and of Cl^- ions with Ar atoms

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Self-consistent-field and configuration-interaction potentials proposed for the $H^- + He$, $Br^- + He$, and $Cl^- + Ar$ systems are tested by comparing measured values of the mobility and diffusion coefficients describing ion motion in gases with those calculated from the potentials and the two- and three-temperature kinetic theories. Tests are also made of the ion-atom potentials derived for these systems from scattering measurements with ion beams.

I. INTRODUCTION

Knowledge of the potential energy of interaction of a negative ion with a neutral atom is important for the determination of the mechanism of electron detachment in collisions between the two. One mechanism dominates if the ionic AB^- potential curve crosses into the AB continuum, and another dominates if the potential only passes close to the continuum.[1-4] Olson and Liu[5-7] have therefore carried out a number of *ab initio* quantal calculations of ion-atom potential energy curves. Since accuracies of such *ab initio* calculations are difficult to assess, independent checks are desirable. There now exists a substantial body of data[8,9] on gaseous ion transport coefficients that can be used for this purpose, since an accurate kinetic theory is now available[10-12] relating the ion-atom interaction potential to the transport coefficients.

We report here on the use of mobility and diffusion data for H^- and Br^- in He and for Cl^- in Ar to check the accuracy of some of the *ab initio* results. The latter consist of self-consistent-field (SCF) calculations for all three systems,[5,6] plus a presumably more accurate configuration-interaction (CI) calculation for H^- with He.[7] For completeness, we also make comparisons with ion-atom potentials derived from scattering measurements with ion beams, consisting of some older results[13] on $H^- + He$ that were used in an early analysis of electron detachment,[14] plus some more recent results[15] on $Br^- + He$ and $Cl^- + Ar$.

II. CALCULATIONS

The interaction potentials derived from scattering measurements on $H^- + He$, $Br^- + He$, and $Cl^- + Ar$ are exponential-repulsive functions of the form

$$V(r)=A\exp(-\alpha r)\ . \tag{1}$$

Values of the parameters A and α are given in Table I, along with the range of separations r in which Eq. (1) is expected to be accurate. For functional potentials such as Eq. (1), O'Hara and Smith

TABLE I. Potential parameters and range of accuracy of the ion-atom potentials derived from beam-scattering measurements.

System	$A\,(e^2/a_0)$	$\alpha(a_0^{-1})$	Range of $r\,(a_0)$	Ref.
$H^- + He$	0.665	1.078	1.5–3.8	13
$Br^- + He$	13.4	1.545	2.6–4.0	15
$Cl^- + Ar$	54.02	1.593	3.4–4.8	15

have developed[16–18] a computer program for efficiently calculating the transport cross sections to a preselected level of accuracy. However, the SCF and CI potentials discussed in this paper are given in the form of pairs of values (V,r). We have therefore used a modification[19] of the O'Hara-Smith algorithm that is capable of handling either functional potentials or tabulated potentials. The transport cross sections have been calculated to an accuracy of 0.5%.

The procedures for calculating the transport coefficients from the transport cross sections have been described elsewhere[10–12,19] and need not be repeated here. The present calculations were carried out to as high as fifth approximation in either the two- or three-temperature theories,[10–12] with the mobilities being calculated to an accuracy of 1% and the diffusion coefficients to an accuracy of 5%.

III. RESULTS

A. $H^- + He$

For this system the attractive well of the potential is so shallow that the transport coefficients at 300 K are completely dominated by the repulsive wall of the potential.[20] We therefore expect the mobility to decrease with increasing electric field strength, the rate of decrease being a rough measure of the steepness of the repulsion.[21] For example, the mobility decreases as $(E/N)^{-1/2}$ for rigid spheres, where E is the electric-field strength and N is the neutral gas number density. The decrease is less rapid for "softer" repulsions, with the mobility remaining constant for potentials varying as r^{-4}.

The experimental mobilities[8,22] are compared in Fig. 1 with those calculated from both the SCF (Ref. 5) and CI (Ref. 6) potentials of Olson and Liu, as well as from a potential (Table I) obtained from an analysis[14] of ion-beam scattering experiments.[13] It is apparent that the SCF potential is too large, since it yields a low mobility, whereas the CI potential gives much better agreement. Insofar as the rate of decrease of the experimental results with E/N can be considered reliable, both *ab initio* potentials appear to be slightly too steep. Although the range of validity[19] of the mobilities calculated from the beam potential does not quite overlap that of the mobility data, a short extrapolation indicates that the beam potential is too small (i.e., the predicted mobility is too large).

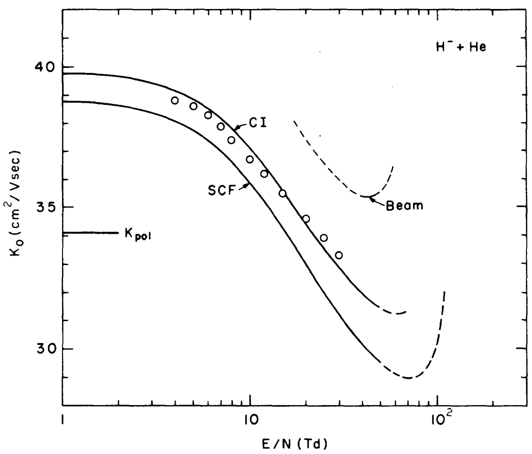

FIG. 1. Comparison of calculated and measured mobilities at 300 K and standard gas density for $H^- + He$ as a function of E/N. For reference, the limiting polarization value of the mobility K_{pol} corresponding to the mobility at 0 K and $E/N = 0$, is also shown. The dashed part of the beam curve at smaller E/N is an extrapolation. A runaway phenomenon is predicted to occur for E/N greater than about 50 Td, above which all curves are shown dashed.

The calculated mobilities show a peculiar behavior for values of E/N greater than about 50 Td ($1\ \mathrm{Td} = 10^{-21}\ \mathrm{V\,m^2}$). The mobility begins to increase, and eventually the mathematical calculations become unstable and diverge. The physical reason for this behavior is that the repulsive potential at high collision energies is so soft that the collisions become unable to absorb all of the momentum acquired by the ions from the electric field between collisions. The ions then accelerate and a runaway phenomenon results. This phenomenon was predicted earlier[23] for H^+ in He, and was subsequently observed experimentally.[24] All three potentials used for H^- in He predict runaway.

The mobility measurements of this system give information on the potential only over the comparatively short range from about 4.3 to $5.8a_0$, or only up to interaction energies of about 0.23 eV, since the measurements did not extend to high E/N. Indeed, the runaway phenomenon would appear to preclude mobility measurements at high E/N, should they be attempted.

Diffusion coefficients have not been measured for $H^- + He$, but values accurate to about 10% can be calculated from the measured mobility and its derivative with respect to E/N, according to generalized Einstein relations.[25] Both parallel $(D_{\parallel})$ and perpendicular $(D_{\perp})$ diffusion coefficients can be obtained, and the values are compared in Fig. 2

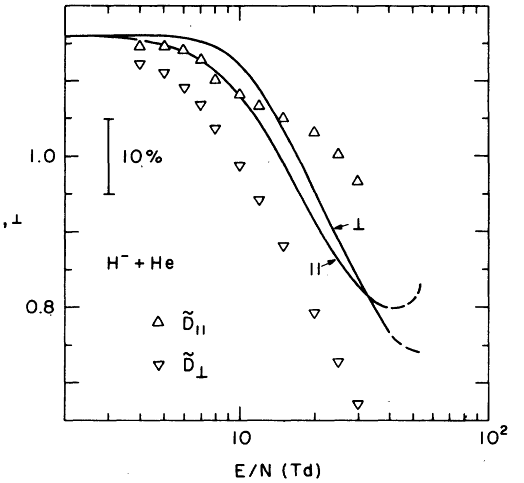

FIG. 2. Comparison of reduced parallel and perpendicular diffusion coefficients for H⁻ + He at 300 K as a function of E/N. The points are not direct measurements, but are calculated from measured mobilities through generalized Einstein relations.

with those calculated from the CI potential. The comparison is conveniently made in terms of reduced coefficients, defined as

$$\tilde{D}_{\parallel,\perp} \equiv qD_{\parallel,\perp}/K_{\rm pol}kT_{\rm pol}\,, \tag{2}$$

$$kT_{\rm pol} \equiv kT + \tfrac{1}{3}M(K_{\rm pol}E)^2\,, \tag{3}$$

where q is the ionic charge, $K_{\rm pol}$ is the mobility the ions would have if the potential were a pure r^{-4} polarization (that is, $K_{\rm pol}$ is the mobility at $T=0$, $E/N=0$), and $T_{\rm pol}$ is a corresponding effective ion temperature at the actual values of T and E/N. This reduction removes the strong increase of $D_{\parallel,\perp}$ with E/N, which goes roughly as $(E/N)^2$. The agreement shown in Fig. 2 is roughly comparable to that for the mobility (Fig. 1), except for larger uncertainties in the $\tilde{D}_{\parallel,\perp}$ than in K_0. Note that the runaway effect is also evident in the calculated diffusion coefficients. The comparison in Fig. 2 is not really an additional test of the potential, but is more a check on the internal consistency of the calculations and the generalized Einstein relations.

B. Br⁻ + He

This system is similar to H⁻ + He in that its attractive well is shallow,[6] so the transport coefficients at 300 K are dominated by the repulsive wall. The experimental mobilities[9,26] are compared in Fig. 3 with those calculated from the SCF potential of Olson and Liu,[6] as well as from a potential (Table I) derived from ion-beam scattering experiments.[15] The SCF potential exhibits a systematic deviation, showing that it is too large but that it has about the correct steepness. Although the range of validity[19] of the mobilities calculated from the beam potential just barely overlaps that of the mobility data, the agreement is quite good; a short extrapolation of the mobilities from the beam potential is also quite good.

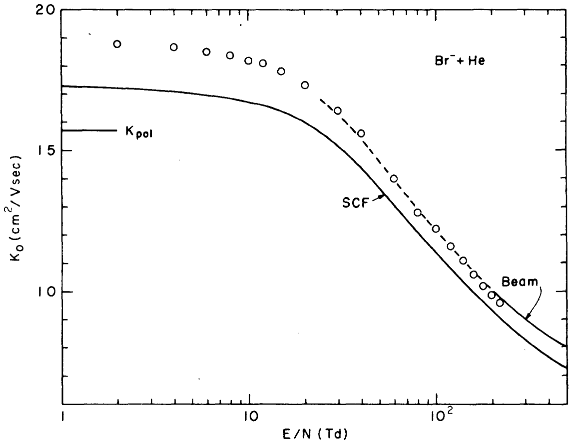

FIG. 3. Comparison of mobilities for Br⁻ + He, legend as in Fig. 1.

The mobility measurements for this system give information on $V(r)$ over the range from about 3.9 to $5.8a_0$, corresponding to interaction energies up to about 0.9 eV.

The parallel and perpendicular diffusion coefficients calculated from the two Br⁻ + He potentials are shown in Fig. 4. No experimental measurements of diffusion coefficients for this system have been reported, but values calculated from the mea-

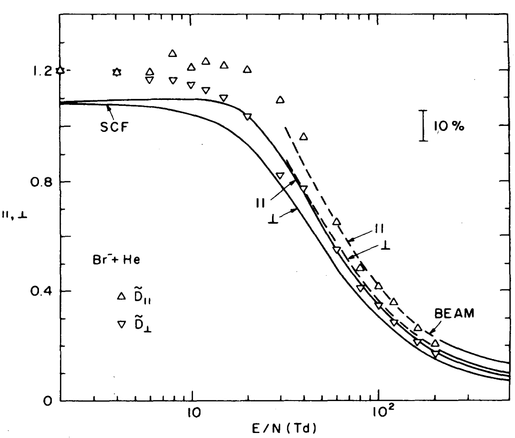

FIG. 4. Comparison of diffusion coefficients for Br⁻ + He, legend as in Fig. 2.

sured mobility by generalized Einstein relations are shown in Fig. 4. The agreement shown in Fig. 4 is comparable to that for the mobility (Fig. 3), except for the larger uncertainties. Again, the comparison is not an independent test of the potentials, but a check on internal consistency through the generalized Einstein relations.

C. Cl$^-$ + Ar

The attractive well is much deeper for this system than for the previous systems, and it has a strong influence on the transport coefficients at 300 K. This is shown not only by the SCF calculations,[5] but also by the distinct maximum in the data. This maximum occurs in the energy range where the repulsive and attractive components of the potential tend to compensate each other—that is, in the region corresponding to the potential well. Model calculations[27] indicate that in the present case the mobility data probe somewhat beyond the position of the potential minimum.

The experimental mobilities[9,28,29] are compared in Fig. 5 with those calculated from the SCF potential of Olson and Liu,[5] as well as from a potential (Table I) derived from ion-beam scattering experiments.[15] From Fig. 5 it is apparent that the mobility probes the repulsive wall of the potential only for E/N greater than about 200 Td. In this region, both potentials give fair agreement with the measured mobilities—the SCF potential is somewhat too large and the beam potential is somewhat too small, but both have about the right steepness.

The potential well has an important influence on the mobility below 200 Td, where Fig. 5 shows that both potentials fail badly. A simple extrapolation of the beam potential gives poor results, because it includes no provision for an attractive well. The SCF potential gives a mobility maximum that occurs at too low a value of E/N (by at least a factor of 2), and that is much too high. The first feature means that the calculated SCF potential well is too shallow by about a factor of 2. The second feature means roughly that the "width" of the potential well is too great, or equivalently that the curvature of the potential at the minimum is too small. The SCF calculations were, of course, not designed to give the potential well accurately.

The parallel and perpendicular diffusion coefficients calculated from the two Cl$^-$ + Ar potentials are shown in Fig. 6. Also shown in Fig. 6 are the experimental values[9,30] for the parallel diffusion coefficient. Although the beam potential gives results that are rather good at high E/N, the SCF potential gives results that are only fair at best. The conclusions reached above on the basis of the mobility results are fully supported by this comparison as well. In this case the comparison for $\widetilde{D}_{\parallel}$ does furnish an independent test of the potentials, although obviously not as good as the mobility because of the greater experimental uncertainty.

The mobility and diffusion coefficients measured for this system give information on $V(r)$ over the

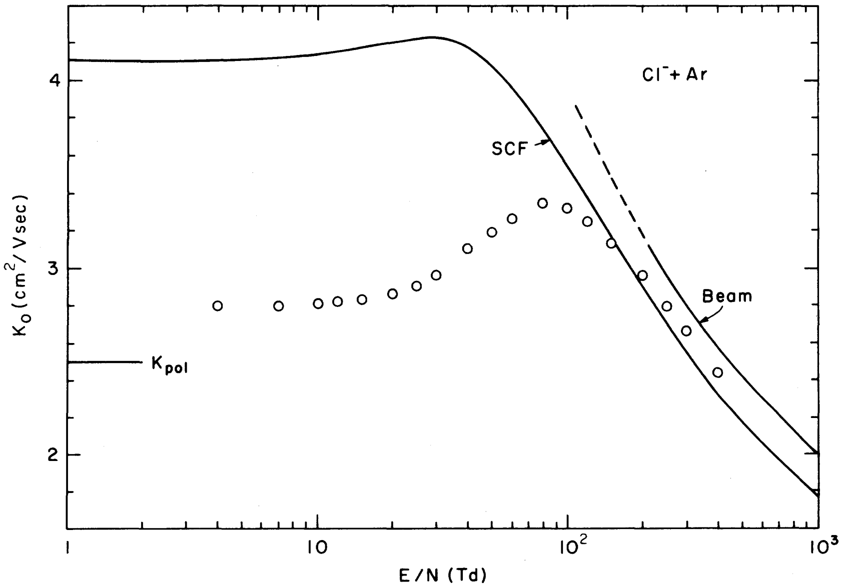

FIG. 5. Comparison of mobilities for Cl$^-$ + Ar, legend as in Fig. 1.

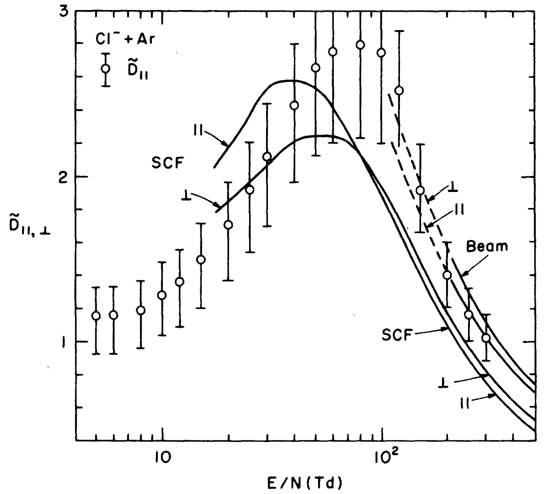

FIG. 6. Comparison of reduced diffusion coefficients for Cl$^-$ + Ar at 300 K as a function of E/N. The open circles with bars represent direct measurements of $D_{\parallel}$.

range from about 4.4 to $10a_0$, corresponding to interaction energies up to about 2 eV on the repulsive wall of the potential.

IV. CONCLUSIONS

We draw the following conclusions from the foregoing comparisons. First, the SCF calculations of Olson and Liu give a reasonable account of the repulsive wall of the potential, although the numerical values they obtain are somewhat too large. In the one case for which CI calculations were performed (H$^-$ + He), the repulsive wall gave excellent agreement with the measured mobilities.

Second, the SCF calculations probably give a poor account of the potential well, although in only one case (Cl$^-$ + Ar) was the well deep enough to affect the experimental transport coefficients appreciably at 300 K. This result is not too surprising, since SCF calculations describe only the long-range r^{-4} polarization component of the attractive potential, and there are other important contributions to the interaction in the well region.[31,32] Olson and Liu did not design their calculations, even the CI ones, with the potential well in mind.[7]

Third, it is not possible to correct the SCF potentials by simply scaling them based upon a comparison of calculated and measured transport properties. This is because they describe the wall reasonably accurately but give a poor account of the well. Improved interaction potentials can only be obtained by an improved CI calculation or by direct inversion[33] of the transport data.

Finally, the ion-beam measurements of the repulsive wall by Kita *et al.*[15] give fair agreement with the transport data at high E/N. Further comparisons between beam and transport data are in progress for a number of other systems.

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[1] A. Z. Devdariani, Zh. Tekh. Fiz. 43, 399 (1973) [Sov. Phys.—Tech. Phys. 18, 255 (1973)].

[2] S. K. Lam, J. B. Delos, R. L. Champion, and L. D. Doverspike, Phys. Rev. A 9, 1828 (1974).

[3] R. L. Champion, L. D. Doverspike, and S. K. Lam, Phys. Rev. A 13, 617 (1976).

[4] J. P. Gauyacq, J. Phys. B 12, L387 (1979).

[5] R. E. Olson and B. Liu, Phys. Rev. A 17, 1568 (1978).

[6] R. E. Olson and B. Liu, Phys. Rev. A 20, 1344 (1979).

[7] R. E. Olson and B. Liu, Phys. Rev. A 22, 1389 (1980).

[8] H. W. Ellis, R. Y. Pai, E. W. McDaniel, E. A. Mason, and L. A. Viehland, At. Data Nucl. Data Tables 17, 177 (1976).

[9] H. W. Ellis, E. W. McDaniel, D. L. Albritton, L. A. Viehland, S. L. Lin, and E. A. Mason, At. Data Nucl. Data Tables 22, 179 (1978).

[10] L. A. Viehland and E. A. Mason, Ann. Phys. (N.Y.) 91, 499 (1975); 110, 287 (1978).

[11] S. L. Lin, L. A. Viehland, and E. A. Mason, Chem. Phys. 37, 411 (1979).

[12] L. A. Viehland and S. L. Lin, Chem. Phys. 43, 135 (1979).

[13] T. L. Bailey, C. J. May, and E. E. Muschlitz, J. Chem. Phys. 26, 1446 (1957).

[14] E. A. Mason and J. T. Vanderslice, J. Chem. Phys. 28, 253 (1958).

[15] S. Kita, K. Noda, and H. Inouye, J. Chem. Phys. 64, 3446 (1976).

[16] H. O'Hara and F. J. Smith, J. Comput. Phys. 5, 328 (1970).

[17] H. O'Hara and F. J. Smith, Comput. Phys. Commun. 2, 47 (1971).

[18] P. D. Neufeld and R. A. Aziz, Comput. Phys. Commun. 3, 269 (1972).

[19] L. A. Viehland (unpublished).

[20] J. H. Whealton, E. A. Mason, and T. H. Vu, Chem. Phys. Lett. 28, 125 (1974).

[21] E. W. McDaniel and E. A. Mason, *The Mobility and Diffusion of Ions in Gases* (Wiley, New York, 1973), Chap. 5.

[22] M. McFarland, D. L. Albritton, F. C. Fehsenfeld, E. E. Ferguson, and A. L. Schmeltekopf, J. Chem. Phys. 59, 6610 (1973).

[23] S. L. Lin, I. R. Gatland, and E. A. Mason, J. Phys. B 12, 4179 (1979).

[24] F. Howorka, F. C. Fehsenfeld, and D. L. Albritton, J. Phys. B 12, 4189 (1979).

[25] M. Waldman and E. A. Mason, Chem. Phys. 58, 121 (1981).

[26] I. Dotan, D. L. Albritton, and F. C. Fehsenfeld, J. Chem. Phys. 66, 2232 (1977).

[27] I. R. Gatland, L. A. Viehland, and E. A. Mason, J. Chem. Phys. 66, 537 (1977).

[28] I. Dotan and D. L. Albritton, J. Chem. Phys. 66, 5238 (1977).

[29] M. G. Thackston, F. L. Eisele, W. M. Pope, H. W. Ellis, I. R. Gatland, and E. W. McDaniel, J. Chem. Phys. 70, 3996 (1979).

[30] F. L. Eisele, M. G. Thackston, W. M. Pope, H. W. Ellis, and E. W. McDaniel, J. Chem. Phys. 70, 5918 (1979).

[31] Ref. 21, Chap. 6.

[32] M. Alvarez-Rizzatti and E. A. Mason, J. Chem. Phys. 63, 5290 (1975).

[33] I. R. Gatland, W. F. Morrison, H. W. Ellis, M. G. Thackston, E. W. McDaniel, M. H. Alexander, L. A. Viehland, and E. A. Mason, J. Chem. Phys. 66, 5121 (1977).