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Interaction potentials and spectroscopy of $Hg^+\cdot Rg$ and $Cd^+\cdot Rg$ and transport coefficients for Hg^+ and Cd^+ in Rg (Rg=He—Rn)

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High-level *ab initio* calculations have been performed on the $Hg^+\cdot Rg$ and $Cd^+\cdot Rg$ species, where Rg=He—Rn. Potential-energy curves have been calculated over a wide range of internuclear separation, sampling the repulsive, equilibrium, and long-range regions. From these curves, rovibrational and spectroscopic constants were derived and compared to those available from previous studies. In addition, transport coefficients were calculated and compared to the available experimental data for the cases of Hg^+ in He, Ne, and Ar. There are two interesting features relating to the mobility results. One is the development of a "mobility minimum" for Hg^+ in the heavier rare gases—with weaker minima being found for Cd^+; a "rule of thumb" is presented for determining when mobility minima might appear. The second is that excellent agreement is found for the direct calculation of mobilities for Hg^+ in ^{22}Ne, and those obtained by scaling the ^{20}Ne mobilities. The latter result allows us to conclude that the mobilities of the various combinations of isotopes can be calculated from the results herein via a mass scaling. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2148955]

I. INTRODUCTION

The mobilities of mercury ions in rare gases (Rg) are important quantities required for the modeling and understanding of discharges and discharge lamps.[1–3] Such values have been available for many years from the measurements of Chanin and Biondi[4] for ground-state Hg^+ in He, Ne, and Ar, with other measurements for Hg^+ in He also being available.[5,6] There appear to be no values available for Hg^+ moving in the heavier rare gases. As far as we can tell, there have been no measurements for ground-state Cd^+ in rare gases, although there have been some related measurements for the $6\,^2P_{3/2}$ excited state[7] in He, and in that work a ground-state mobility was estimated to be 20 $cm^2\,V^{-1}\,s^{-1}$ at 760 Torr and 300 K.

In previous work, we have employed high-quality *ab initio* interatomic potentials to calculate transport coefficients for the complete set of 36 alkali-metal cation/rare-gas combinations.[8–11] These are all closed-shell systems that serve as prototypes of cation/rare-gas interactions, as discussed in detail by Bellert and Breckenridge.[12] Very recently, we also tackled the more demanding open-shell system of O^- with the three lightest rare gases, where it was shown[13] that it was important to employ potentials which took account of the spin-orbit interaction; this arises owing to the production of $^2\Pi$ and $^2\Sigma^+$ states upon interaction of the O^- with the rare gas, and the interaction between the two $\Omega=1/2$ states thereafter. The cases of Hg^+ and Cd^+ interacting with a rare gas in some ways fall between the previous two situations, since each metal cationic complex is an open-shell $^2\Sigma^+$ state [Hund's case (a)], and so there is no spin-orbit interaction to first order (and the excited states are far enough away that any higher-order effects are small). Consequently, a single-reference molecular-orbital method should be adequate for this system. We therefore elect to use the RCCSD(T) method, as we employed in our previous work. The aim is to produce interatomic potential-energy curves that are of high quality in all regions: near the minimum in order to obtain accurate spectroscopic constants, and at short and long ranges in order to obtain accurate mobilities over a wide range of E/N (the ratio of the electric field to the number density). As we have noted in our previous work, in some ways the accurate calculation of mobilities from a potential is a more stringent test than the usual spectroscopic parameters, since it requires an accurate potential everywhere, rather than just close to the minimum.

There are data available[12] for $Hg^+\cdot Rg$ for Rg=Ne, Ar, Kr, and Xe, whereas for $Cd^+\cdot Rg$, only the Rg=Ar system has been studied much previously. Consequently, the calculation of interatomic potentials for all 12 systems ($Hg^+\cdot Rg$ and $Cd^+\cdot Rg$) will provide a large amount of information on these systems for the first time. We can then assess the ac-

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curacy of the potentials against the previous work, where it is available. Since the majority of information is available on the $Hg^+ \cdot Rg$ species, we first briefly summarize that.

The most detailed information appears to be that arising from a study of fairly high-lying *ns* Rydberg states of Hg·Ne and Hg·Ar by Onda *et al.*[14] and Onda and Yamanouchi[15] who employed optical-optical double-resonance (OODR) spectroscopy to reach these levels. Information was obtained on both triplet and singlet levels, each corresponding to an *ns* Rydberg electron and a $Hg^+(^2S)$ atomic core, with the rare-gas atom able to be positioned inside or outside the Rydberg orbit. The highest state $(n=10)$ for Hg·Ne yielded spectroscopic constants, which are expected to be close to those of the ion; for Hg·Ar, the $n=7$ and 8 triplet states were studied. Emission from $Hg^+ \cdot Ar$ was recorded by Bridge[16] and analyzed to yield various rotational and vibrational spectroscopic parameters, as well as the dissociation energy; the analysis was performed with the aid of a model for Hund's case (c) coupling reported by Hougen.[17] $Hg^+ \cdot Ar$ was also studied by Linn *et al.* by direct photoionization,[18] where the dissociation energy was deduced. In a similar study, Liao and Ng[19] obtained dissociation energies of $Hg^+ \cdot Kr$ and $Hg^+ \cdot Xe$. We note that Bellert and Breckenridge[12] made small modifications to the photoionization values in compiling their review (and it is these modified values that we employ in the present work). There appear to be no data available for $Hg^+ \cdot He$ or $Hg^+ \cdot Rn$. We shall discuss the previous data when comparing to our own below.

For $Cd^+ \cdot Rg$, there only appear to be estimated values available for $Cd^+ \cdot Ar$, derived by Bellert and Breckenridge[12] from parameters for the first triplet Rydberg state;[20,21] we shall compare these values to our own in the discussion below.

II. COMPUTATIONAL DETAILS

A. Methodology

All curves were obtained using the RCCSD(T) method as implemented in MOLPRO;[22] each point was corrected for basis-set superposition error (BSSE) employing the full counterpoise correction. The basis sets used were standard aug-cc-pV5Z ones for He, Ne, and Ar (omitting the *h* functions for Ne or Ar). For Kr, Xe, Rn, and Hg, effective core potential (ECP)-based basis sets were designed to be similar to aug-cc-pV5Z quality in the valence region—these will be described briefly below. For $Hg^+ \cdot He$, $Hg^+ \cdot Ne$, and $Hg^+ \cdot Ar$, we also made limited calculations employing the *d*-aug-cc-pV5Z basis sets for the rare gas, including the *h* functions for Ne and Ar.

For Hg^+ we employ the same basis sets we used for work[23] on $Hg \cdot H_2O$ and $Hg^{2+} \cdot H_2O$, where the basis sets were described in full; we also employed these basis sets for our study of the $HgCH_3$ and $HgCH_3{}^+$ species.[24] The ECP60*M*WB effective core potential[25] (where the *M* indicates that the neutral atom is used in the derivation of the ECP and WB implies the use of the quasirelativistic approach described by Wood and Boring[26]) was used, which treats 60 electrons as core (up until the 4*f* shell). The $5s^2 5p^6 5d^{10} 6s^2$ electrons were described by valence basis functions, as detailed in Ref. 23, to yield a ECP60*M*WB$[11s10p8d5f4g]$ basis set, which is of the same form as an aug-cc-pV5Z basis set, with the *h* functions omitted. For $Hg^+ \cdot He$, $Hg^+ \cdot Ne$, and $Hg^+ \cdot Ar$, we also performed some scans with a *d*-aug-cc-pV5Z basis set, as mentioned above. In these cases, we added diffuse functions ($\zeta_{s,p}=0.001\,272$, $\zeta_d=0.004\,74$, $\zeta_f=0.009\,329$, and $\zeta_g=0.011\,72$), and a full set of *h* functions ($\zeta=2.5$, 0.714 29, 0.204 08, and 0.058 309).

For Cd^+, we employed the same basis set used in our previous study[27] on $Cd \cdot H_2O$ and $Cd^{2+} \cdot H_2O$—this employs the ECP28*M*WB effective core potential,[25,28] augmented with a $[11s10p8d5f4g]$ valence basis set.

For Kr, the ECP28*M*WB effective core potential[29] was augmented with a $[8s7p5d4f3g]$ valence basis set. The $[8s7p5d]$ part of this basis is the same as used in our study on the polarizabilities of the rare-gas atoms,[30] whereas the *f* and *g* spaces have been expanded by one function of each type, being a set of four even-tempered *f* functions ($\zeta=1.5$, 0.5, 0.166 67, and 0.055 556) and three even-tempered *g* functions ($\zeta=1.2$, 0.342 86, and 0.097 959).

For Xe, the ECP46*M*WB effective core potential was employed[29] with $[8s8p5d4f3g]$ valence basis functions. Again, this basis set was as employed in our previous work on polarizabilities,[30] but with the *f* and *g* spaces being expanded by one basis function of each type: four even-tempered *f* functions ($\zeta=1.951\,12$, 0.6728, 0.232, and 0.08) and three even-tempered *g* functions ($\zeta=1.225$, 0.25, and 0.1).

For Rn, a new basis set was designed. This employs the ECP78*M*WB effective core potential[31] augmented with a $[10s8p5d4f3g]$ basis set. The innermost *s* and *p* functions were contracted functions obtained from a $(19s17p)$ even-tempered basis set (middle exponent=1.5, ratio=0.22 for *s*; middle exponent=1.5, ratio=0.3 for *p*), with the contraction coefficients being obtained from a Hartree-Fock calculation on the neutral Rn atom. The other nine *s* and seven *p* functions were uncontracted, and were even-tempered sets (middle exponent=0.2,, ratio=2.0 for *s*; middle exponent =0.15, ratio=2.0 for *p*). The five *d* functions were an even-tempered set with middle exponent=0.18 and a ratio of 3.0, while the four *f* and three *g* functions were even-tempered sets ($\zeta_f=1.2$, 0.4, 0.133 33, and 0.044 444; $\zeta_g=1.2$, 0.3, and 0.075).

Scans were carried out from short to long bond lengths covering the repulsive, equilibrium, and long-range regions, both to ensure that good coverage of the minima was achieved (to obtain reliable spectroscopic parameters) and also to satisfy the demands of the transport property calculations over a large range of E/N.

B. Spectroscopy and interaction parameters

From the interaction potential-energy functions, the equilibrium interatomic separations and the dissociation energies were obtained. LeRoy's LEVEL program[32] was used to calculate the rovibrational energy levels, and the ω_e and $\omega_e x_e$ parameters were then determined from the calculated energy levels by straightforward means.

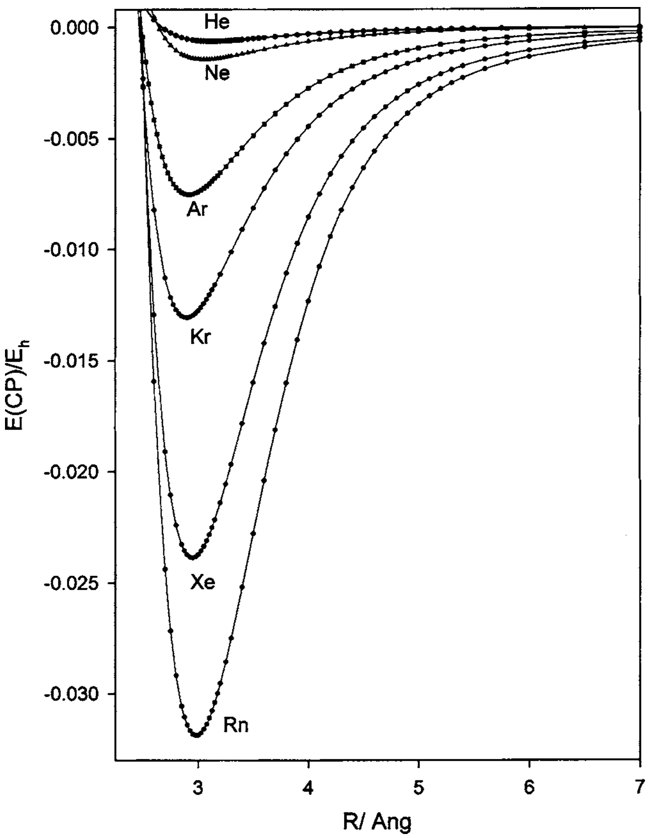

FIG. 1. Potential-energy curves for the $Hg^+ \cdot Rg$ species. See text for details.

The rotational energy levels for each vibrational level were fitted to the expression,

$$E(v,J) = E(v,0) + B_v J(J+1) - D_v J^2(J+1)^2 + H_v J^3(J+1)^3 + \cdots, \quad (1)$$

although the higher-order terms were very small.

C. Transport coefficients

Starting from the interaction potentials, transport cross sections were calculated using the program QVALUES.[33,34] These cross sections were then used in the program GRAMCHAR (Ref. 35) to determine the ion mobility and the other gaseous ion transport coefficients as functions of E/N at particular gas temperatures. The mobilities are generally precise within 0.1%, which means that the numerical procedures within programs QVALUES and GRAMCHAR have converged within 0.1% for the given ion-neutral interaction potential. However, at some intermediate E/N values convergence is sometimes only within a few tenths of a percent and a slight "wobble" is observed in the computed values for the heavier rare gases. The diffusion coefficients are generally precise within 1%, with the exception of intermediate E/N values where convergence is only within 3%.

III. RESULTS AND DISCUSSION

In Figs. 1 and 2, we present the interaction potentials in the well region and at large separations for $Hg^+ \cdot Rg$ and $Cd^+ \cdot Rg$. In Tables I and II, we present the calculated spectroscopic quantities for these species. We first discuss these spectroscopic quantities and compare to other available values, before moving onto the transport properties.

A. Spectroscopic quantities for $Hg^+ \cdot Rg$

We commence by discussing the results for $Hg^+ \cdot Ne$, since it is the lightest species for which there appears to be reliable experimental spectroscopic data to which to compare, albeit from Rydberg states. As noted in the Introduction, Onda *et al.*[14] and Onda and Yamanouchi[15] studied both singlet and triplet states of $Hg \cdot Ne$, arising from $Hg^+(^2S)ns$, where n ranged from 6-10. Bellert and Breckenridge[12] have recommended spectroscopic parameters for $Hg^+ \cdot Ne$ based on these studies, and these are presented in Table I alongside our calculated values. First it may be seen that the result of addition of the diffuse functions on the Ne atom has a small, but significant effect on the calculated properties, bringing them in better line with the recommended values, in the main. In fact, the overall agreement is really very good, and we conclude that the potential with the diffuse functions added is very reliable, at least for spectroscopic parameters. In addition, we know from our work on the polarizabilities of the rare gases[30] that adding one set of diffuse functions gives a significant increase in the accuracy of the calculated dipole polarizability (and second hyperpolarizability) of the Ne atom, and so is expected to improve the accuracy of the description of the interaction here.

For $Hg^+ \cdot Ar$, in addition to Rydberg state[14] and photoionization studies,[18] there has also been a direct spectroscopic study,[16] employing rotationally resolved ultraviolet emission. We collect the data in this study and the recommended values of Ref. 12 in Table I. The agreement between our calculations and the measured data from Ref. 16 is extremely good with the diffuse functions making small changes, which bring each quantity into slightly better agreement with the experiment. The quantity with which there is the greatest spread of previously reported values is the dissociation energy D_e. The lowest value is 1630 ± 100 cm^{-1} derived from a Birge-Sponer extrapolation employing the spectroscopic constants ω_e and $\omega_e x_e$ in the ultraviolet emission study;[16] a value of 1890 ± 140 cm^{-1} is obtained from the value of 1840 ± 140 obtained for D_0 in the photoionization study[18] of Linn *et al.* and corrected for zero-point energy of ca. 50 cm^{-1}. Note that Bellert and Breckenridge[12] suggest that the values of Ref. 18 should be lowered by ~ 80 cm^{-1} to account for the field shift of the ionization energy, from which the D_0 value was derived, giving a value of $D_e = 1810 \pm 140$ cm^{-1}. A value of 1775 cm^{-1} for (presumably) D_0 is reported in a mass-resolved resonance-enhanced ionization study by Martrenchard-Barra *et al.*,[36] which would suggest a D_e value of 1825 cm^{-1}. The two values we derive in the present work suggest that it is difficult to differentiate between the experimental values, given the significant errors. If the recommended value of Ref. 12 had a slightly larger error bar, then our best calculated value would be in agreement; it seems likely that the present value is the most accurate available. The close agreement of the vibrational quantities with the ultraviolet study, and the rotational parameters gives added confidence in our calculated potential. We also

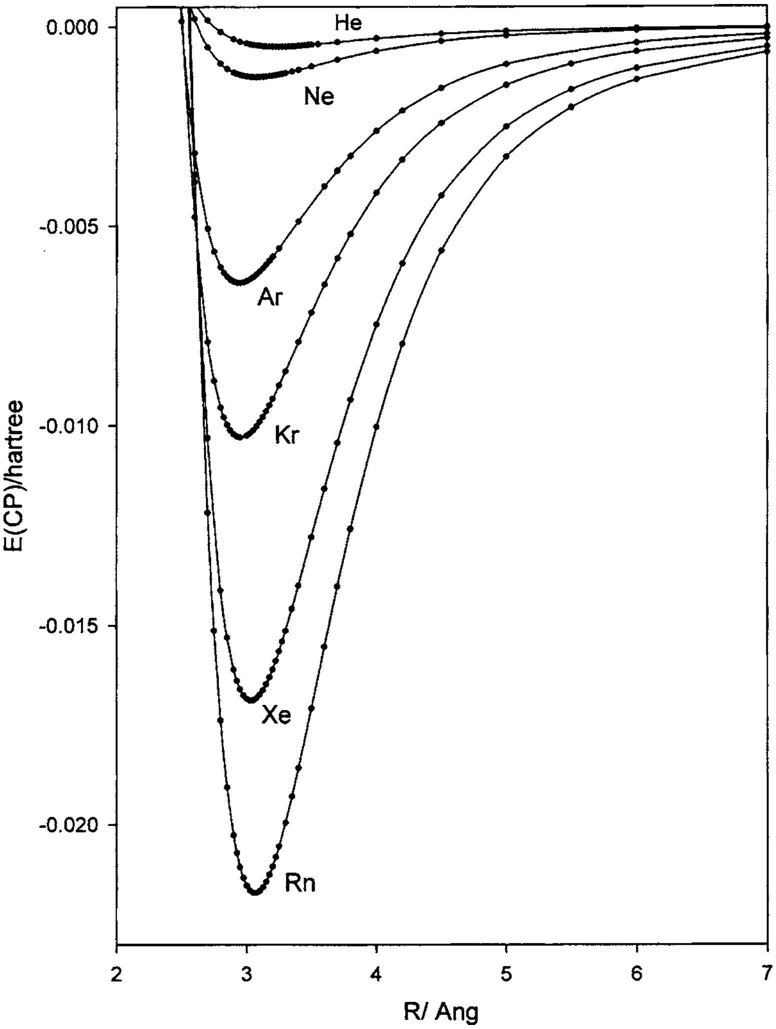

FIG. 2. Potential-energy curves for the $Cd^+ \cdot Rg$ species. See text for details.

note that the first centrifugal distortion constant derived from the rotational analysis of Ref. 16 is $(9.78 \pm 0.20) \times 10^{-8}$ cm^{-1}, which is in excellent agreement with the values of 9.94×10^{-8} and 9.78×10^{-8} cm^{-1}, obtained here with and without the diffuse functions, respectively.

For $Hg^+ \cdot Kr$ and $Hg^+ \cdot Xe$, only estimated values of the bond lengths are available, with dissociation energies being derived from the photoionization studies of Liao and Ng.[19] Their D_0 values of 0.393 ± 0.013 eV $(3170 \pm 100\ cm^{-1})$ and 0.748 ± 0.013 eV $(6030 \pm 100\ cm^{-1})$ were decreased[12] by ~ 80 cm^{-1} "to account for apparent field-ionization lowering of the ionization energy," and presumably then corrected to a D_e value. Given the uncertainties surrounding these values, the agreement of our calculated D_e value and the value recommended by Bellert and Breckenridge (see Table I) is satisfactory, but we believe our value is likely the more reliable, since the D_e value for $Hg^+ \cdot Xe$ is also in rather poorer agreement. The fact that both D_e values for $Hg^+ \cdot Kr$ and $Hg^+ \cdot Xe$ are too high is suggestive that the ionization energies of the Hg·Kr and Hg·Xe species determined in Ref. 19 are too low. In photoelectron spectra of refractory species, such an observation is usually explained by the presence of hot bands, which contribute to the low ionization energy region of the spectrum. For $Hg^+ \cdot Kr$, this may be a plausible explanation, but the size of the difference is a little surprising and is perhaps suggestive of other factors playing a role. The fact that the $Hg^+ \cdot Xe$ value is almost 800 cm^{-1} too low is a more definitive indication that some other explanation is called for.

In order to test the $Hg^+ \cdot Xe$ potential further, we carried out single-point calculations, at 2.95 Å, adding first an extra set of diffuse functions (of each angular momentum), to make a "*d*-aug-cc-p V5Z" type basis set for Xe, and separately, adding in two *h* functions $(\zeta = 1.0$ and $0.33)$ for Xe. These gave D_e values of 5240 and 5285 cm^{-1}, respectively. We also employed a smaller core ECP, using the ECP28*M*WB potential, together with an aug-cc-pV5Z valence basis for Xe,[37] but correlating the same 18 electrons as with the larger-core ECP: this gave a calculated D_e value of 5233 cm^{-1}. Finally, we also correlated the 4*d* electrons, where we added extra tight functions to help describe these $(\zeta_d = 7.2$, 3.6, and 1.8; ζ_f, $\zeta_g = 4.625$ and 1.85, and $\zeta_h = 2.7)$. We obtained a best D_e value of 5357 cm^{-1}. From these values, we deduce that there are no obvious deficiencies in our potential that would raise the calculated dissociation energy to ~ 6000 cm^{-1}, and we conclude that the experimental D_e value is too high. This is in agreement with the experimental value of D_e being too high for $Hg^+ \cdot Ar$, as discussed above. One plausible reason for this would be the presence of higher-order clusters, $Hg \cdot (Ar)_n$, which could fragment after ionization, yielding ions that appear in lower-mass channels,

TABLE I. Calculated spectroscopic parameters for Hg$^+\cdot$Rg. [The values of Ref. 12 are given as the "experimental values," and are those recommended in that work—for a discussion of the original work see that reference, and the text herein. The exception is for Hg$^+\cdot$Ar where both the recommendations of Ref. 12 and the results of Bridge (Ref. 16) are given, as the latter work contains more detailed information than covered in the compilation of Ref. 12.]

Species	Basis set[a]	R_e/Å	D_e/cm^{-1}	B_0/cm^{-1}	α_e/cm^{-1}	0-1	ω_e	$\omega_e x_e$
Hg$^+\cdot$He	aug-cc-pV5Z	3.12	138	0.407	⋯	51.3	71.9	10.30
	d-aug-cc-pV5Z	3.10	144	0.413	⋯	53.2	74.3	10.55
Hg$^+\cdot$Ne	aug-cc-pV5Z	3.06	316	0.0966	5.06×10^{-3}	49.3	54.8	2.77
	d-aug-cc-pV5Z	3.04	334	0.0982	5.01×10^{-3}	51.4	57.0	2.81
	Exp.	2.98 ± 0.03[b]	346[b]				57.8 ± 1.0[b]	
Hg$^+\cdot$Ar[c]	aug-cc-pV5Z	2.91	1650	0.0590	9.37×10^{-4}	89.9	92.9	1.49
	d-aug-cc-pV5Z	2.90	1720	0.0598	9.31×10^{-4}	92.4	95.4	1.50
	Expt.	2.868[d,e]	1630 ± 100[e]	0.0614[e]		97.4[e]	99.0[e]	1.5[e]
		2.86 ± 0.01[b]	1790 ± 100[b]					
Hg$^+\cdot$Kr		2.89	2867	0.0338	2.85×10^{-4}	90.4	92.0	0.80
	Expt.	[2.8][b]	[3150 ± 150][b]					
Hg$^+\cdot$Xe		2.95	5237	0.0243	1.13×10^{-4}	99.8	100.7	0.44
	Expt.	[2.8][b]	6020 ± 150[b]					
Hg$^+\cdot$Rn		2.98	6997	0.0179	5.96×10^{-5}	94.6	95.2	0.27

[a] See text for description of basis sets.

[b] Reference 12.

[c] The distortion constant for Hg$^+\cdot$Ar from the ultraviolet emission study (Ref. 16) is $(9.78\pm0.20)\times10^{-8}$ cm^{-1}, while the two calculated values are 9.94 and 9.78×10^{-8} cm^{-1} for the "no diffuse" and "diffuse" calculations, respectively.

[d] This is actually an R_0 value, the R_e value is expected to be ca. 0.01 Å shorter (~2.86 Å, cf. Ref. 12).

[e] Reference 16.

such as Hg$^+\cdot$Ar. Indeed, the photoionization study of Martrenchard-Barra *et al.*[36] looked at such fragmentation processes, and reported observing spectra in lower-mass channels. This being the case, one may hypothesize that in the study of Linn *et al.*,[18] such cross contamination of spectra has occurred. This would suggest that the ionization energy of Hg$\cdot$Ar reported by Linn *et al.* was too low, but interestingly Martrenchard-Barra *et al.*[36] report a value in close agreement based on the extrapolation of Rydberg states (however, this work does not appear to have been published in full). It is also plausible that the electric-field shifts have been underestimated. Thus, although there will inevitably be improvements possible to describe the interactions in these heavy species, we feel that we have examined many of these, and so we conclude that it is likely that the previously reported D_e values from photoionization studies are too high, particularly for Hg$^+\cdot$Kr and Hg$^+\cdot$Xe; however, the specific reason for this is unclear.

There appear to be no experimental data available for the Hg$^+\cdot$He complex, and none were estimated by Bellert and Breckenridge.[12]

B. Spectroscopic constants for Cd$^+\cdot$Rg

As noted in the Introduction, there appears to be very little experimental data available on the Cd$^+\cdot$Rg species, with the estimated values for Cd$^+\cdot$Ar from Bellert and Breckenridge[12] seemingly being the only available numbers. Given that these were derived from fairly low-lying Rydberg states, the agreement between the calculated values and the experimental ones (see Table II) is good. It is, perhaps, worth pointing out here that the trends in R_e for Hg$^+\cdot$Rg and Cd$^+\cdot$Rg are very similar, with an initial shortening of the internuclear separation (as the attractive terms dominate, and the charge/induced dipole interaction "wins"), followed by an increase as the repulsive interactions start to take over,

TABLE II. Calculated spectroscopic parameters for Cd$^+\cdot$Rg. (The values of Ref. 12 are given as the "experimental values," and are those recommended in that work—for a discussion of the original work see that reference, and the text herein.)

Species		R_e/Å	D_e/cm^{-1}	B_0/cm^{-1}	α_e/cm^{-1}	0-1	ω_e	$\omega_e xe$
Cd$^+\cdot$He		3.24	108	0.381	⋯	41.7	59.4	8.85
Cd$^+\cdot$Ne		3.07	276	0.102	5.72×10^{-3}	43.9	48.9	2.47
Cd$^+\cdot$Ar		2.94	1408	0.0652	1.21×10^{-3}	83.4	86.5	1.55
	Expt.	[2.87][a]	[1525][a]				[88][a]	
Cd$^+\cdot$Kr		2.96	2260	0.0397	4.28×10^{-4}	83.8	85.6	0.92
Cd$^+\cdot$Xe		3.03	3705	0.0299	1.98×10^{-4}	92.0	93.2	0.60
Cd$^+\cdot$Rn		3.06	4763	0.0238	1.19×10^{-4}	91.1	92.0	0.43

[a] Reference 12.

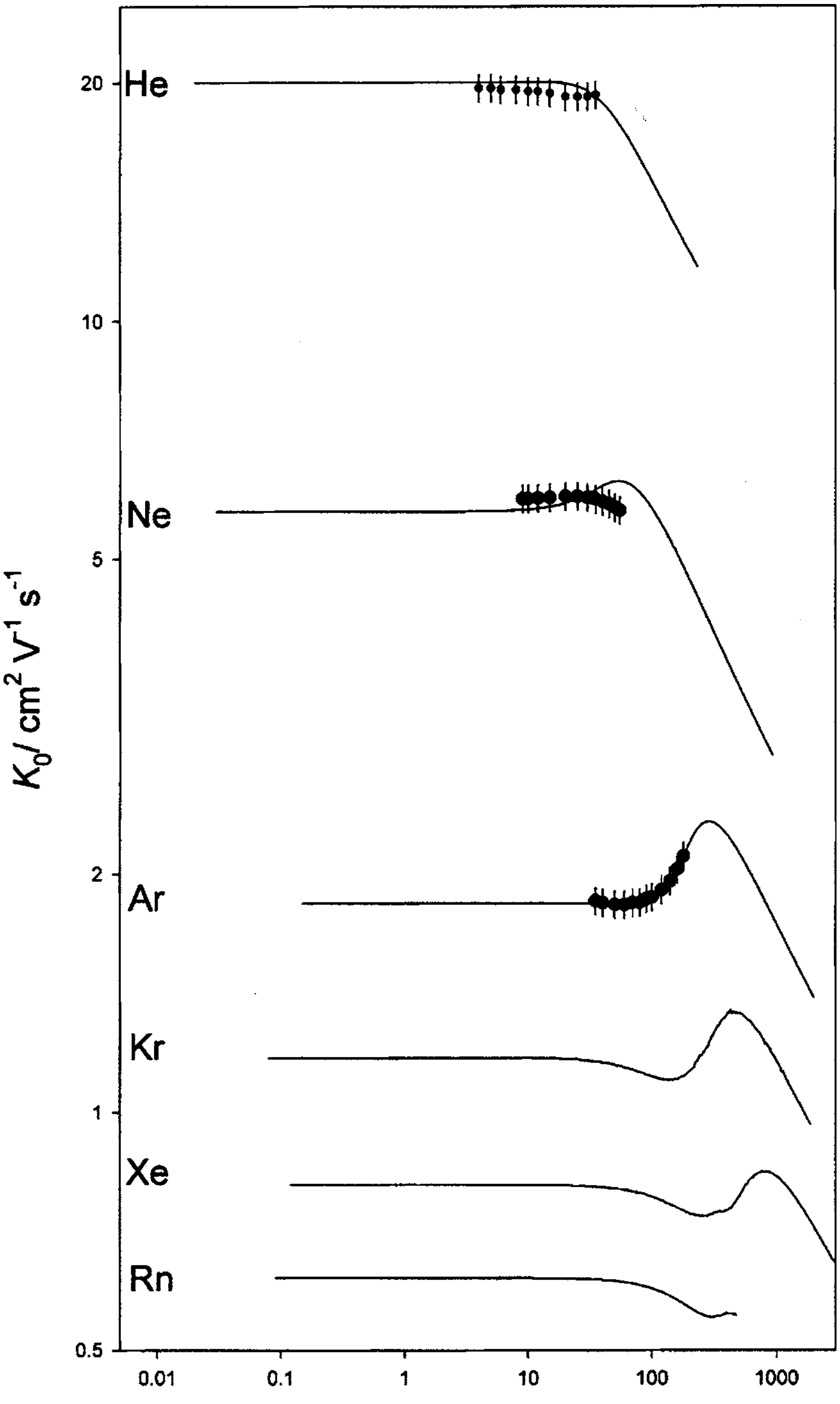

FIG. 3. Standard mobility data for Hg^+ in Rg (log-log plot). The experimental data have a cited error of 4%, and were originally reported in Ref. 4, but the smoothed version of these data (reported in Ref. 38) was employed. See text for details. Note that the bumpiness in the cases of Hg^+ in Xe and Rn is an artifact of the mobility calculations—it is possible to remove this by tighter convergence.

owing to the size and number of electrons on the Rg atom. This sort of effect is often seen in $M^+ \cdot Rg$ species.

C. Transport coefficients for $Hg^+ \cdot Rg$ and $Cd^+ \cdot Rg$

The results of the comparison of the calculated standard mobilities K_0 and the experimental ones (smoothed versions of the data of Ref. 4, reported in Ref. 38) are given both graphically (Fig. 3) and statistically (Table III). The differences between the measured and calculated transport coefficients were determined graphically and by using statistical quantities δ and χ, which take into account the estimated errors in each quantity.[35] If the experimental and calculated errors are the same at all E/N, then δ is the ratio of the average percentage difference to the maximum combined percentage difference expected, while χ is the ratio of the standard deviation of the percentage differences to the root mean square of the maximum combined percentage deviations expected. A positive value of δ indicates that the data lie above the calculated values, and vice versa. Values of $|\delta|$ that are substantially lower (alternatively, higher) than 1 indicate that there is substantial agreement (disagreement) between the calculated and measured values on average. Values of χ that are not much larger than $|\delta|$ indicate that there is little scatter in the experimental data and that the agreement between the calculated and measured values is uniform over

TABLE III. Statistical comparison of calculated and experimental transport data for Hg^+ in He, Ne, and Ar (A is the accuracy cited for the experiment—but note that it is likely that this is too optimistic (see text) and P is the precision of the calculations).

Data type	Potential	E/N in Td	No. of points	A(%)	P(%)	δ	χ
$Hg^+ \cdot He$	aug-cc-pV5Z	4.0-35.0	11	4	0.1	−0.730	0.762
	d-aug-cc-pV5Z	4.0-35.0	11	4	0.1	−0.525	0.588
$Hg^+ \cdot Ne$	aug-cc-pV5Z	9.0-55.0	12	4	0.1	−0.800	1.322
	d-aug-cc-pV5Z	9.0-55.0	12	4	0.1	−0.300	1.054
$Hg^+ \cdot Ar$	aug-cc-pV5Z	35.0-180.0	12	4	0.1	0.090	0.123
	d-aug-cc-pV5Z	35.0-180.0	12	4	0.1	⋯	⋯

all values of E/N, while values of χ substantially greater than $|\delta|$ indicate that at least one of these factors is not true.

Diffusion coefficients and mobilities have been calculated over wide ranges of E/N and at a variety of temperatures, and we have placed the results in the gaseous ion transport database at Chatham College.[39] Here, we will only discuss the mobility results since there have been no experimental determinations of diffusion coefficients for these systems. As may be seen from the statistical results in Table III, and also from the more visual form of the data in Fig. 3, the agreement between the calculated data and the experimental data is reasonably good for Hg^+ in He, in that the calculated curves almost passes through the experimental error bars. The agreement of the curve calculated with the additional sets of diffuse functions (the one that is shown in the figure) is slightly better than the one without, but this is not significantly better agreement with the experimental data, bearing in mind the size of the error bars. This is mirrored in the absolute value of δ being <1. It can be noticed that the experimental data appear to show a slight dip which would be unusual for a system involving helium, but this dip does not seem to be too significant within the experimental error bars, and such a dip does not occur in the calculated curve. [The experimental data are probably less accurate than the 4% originally claimed, given that it was only with subsequent improvements in the Pittsburgh selected ion drift apparatus that data of 3%–5% accuracy could be reliably obtained (see pages 68–69 of Ref. 40).]

We now move onto looking at the $Hg^+ \cdot Ar$ system, where the agreement between the experimental data and the calculated curve is excellent (see Fig. 3), as also demonstrated by the very low value of δ, and also by the very similar χ value. What is exceptional about the calculated curve is that it passes almost directly through the midpoint of the each experimental error bar. We did not pursue this system further by calculating mobilities from a potential-energy curve where further diffuse functions had been added to the basis set, since these calculations were very expensive. Note that we did calculate the curve around the minimum using this larger basis set and calculated spectroscopic parameters, as described above. The agreement between the quantities calculated with the two basis sets was very good, and we do not expect any great deviations would be observed if mobilities were calculated with a complete potential, obtained with the additional diffuse functions.

The worst agreement is that of Hg^+ in Ne, where the calculated curve is actually rising where the experimental data are falling. As discussed in Ref. 30, the polarizability of Ne appears to be more demanding to calculate accurately than the other rare gases, but we showed that a doubly augmented quintuple-ζ basis set gives a good performance. In fact, the mobility curve calculated using the doubly augmented basis set is not too much different from the mobility curve calculated with the basis without the extra diffuse functions, although the statistics are slightly better. Given the

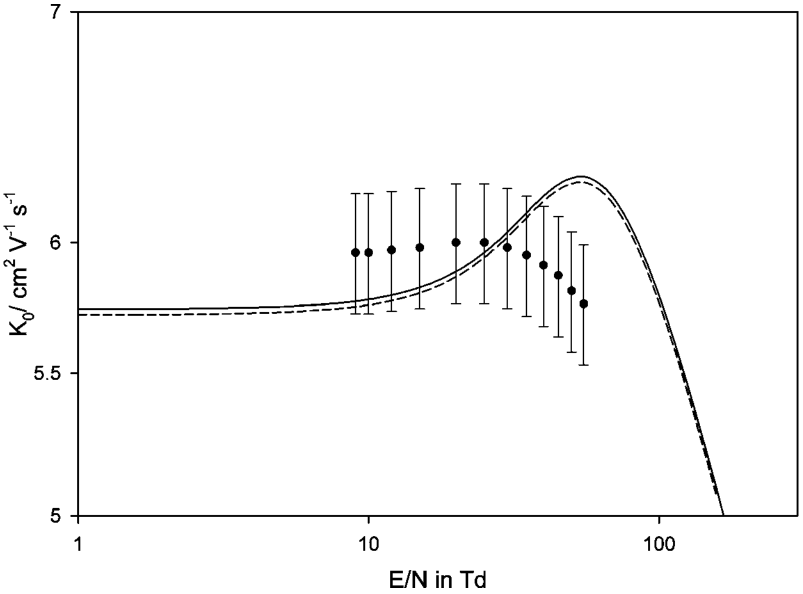

FIG. 4. Comparison of the reduced mobility of Hg′ in pure ^{20}Ne (dashed line) and a mixture of 90.48% ^{20}Ne and 9.52% ^{22}Ne (solid line).

good performance of the basis set for the spectroscopy of $Hg^{+}\cdot Ne$ and the results for the other systems, plus our knowledge of the performance of this basis set for the polarizability, we are confident that the calculated data are reliable, and so considered another possibility for the disagreement with the experimental data. Unlike He and Ar, for which there is an extremely dominant isotope (>99.9% ^{4}He and 99.6% ^{40}Ar), there are two isotopomers of neon with significant abundances: 90.48% ^{20}Ne and 9.25% ^{22}Ne (with a very small amount of ^{21}Ne): We therefore calculated the mobility of Hg^{+} in a sample of 90.48% ^{20}Ne and 9.52% ^{22}Ne (note that we combine the ^{21}Ne and ^{22}Ne together as mass 22—this should slightly emphasize any differences). This is achieved by making use of Blanc's Law,[40,41] which states that

$$\frac{1}{K_{\mathrm{mix}}}=\frac{x_1}{K_1}+\frac{x_2}{K_2}, \tag{1a}$$

where the K_i are the mobilities of an ion in each of the isotopically pure gases, and the x_i are their corresponding mole fractions; K_{mix} is the mobility of the ion in the mixture of isotopes. This law has been tested thoroughly.[42]

The results are shown in Fig. 4, where we also show the results for pure ^{20}Ne. As may be seen, the changes are minimal, and do not explain the discrepancies between experiment and theory. We therefore conclude that there is some anomaly with the experimental data, and certainly it would be beneficial to perform additional mobility measurements on this system. We comment on the effect of isotopes on mobilities further below.

For the three heaviest systems, there are no experimental data to which to compare. However, an interesting observation is the development of mobility minima between 100-1000 Td ($1\ \mathrm{Td}=10^{-17}\ \mathrm{V\,cm}^2$). Such a minimum has been observed experimentally in a number of cases, such as for O^{+} in Ar (Ref. 43) at close to room temperatures, and Ar^{+} in He at 4.35 K.[44,45] The appearance of mobility minima have been discussed in the books by Mason and McDaniel.[40,46] As demonstrated therein, the appearance of a mobility minimum appears to derive from a substantial R^{-6} term (and higher terms), leading to the potential being significantly more attractive than that caused by the charge/induced-dipole interaction (which we shall term V_{pol}). In Fig. 5, we show the V_{pol} potential term, and the full counterpoise-corrected interaction energy, for the cases of $Hg^{+}\cdot He$ and $Hg^{+}\cdot Kr$. As may be seen, V_{pol} crosses the interaction potential more or less at R_e for $Hg^{+}\cdot He$, but at separations significantly shorter than R_e for $Hg^{+}\cdot Kr$. Thus, in the region of just less than R_e to long range, the counterpoise (CP)-corrected interaction potential is significantly more attractive than V_{pol}, whereas for $Hg^{+}\cdot He$, it is only when $R>R_e$ that this is the case. It therefore seems that if V_{pol} crosses the interaction potential at $R<R_e$, then it is likely that a "mobility minimum" will occur, although the temperature at which it occurs may be quite low, depending on the magnitude of the deviation of the potential from V_{pol}. For Hg^{+} in Ar, a shallow minimum is present in the calculated mobilities, which is not visible in the experimental data.

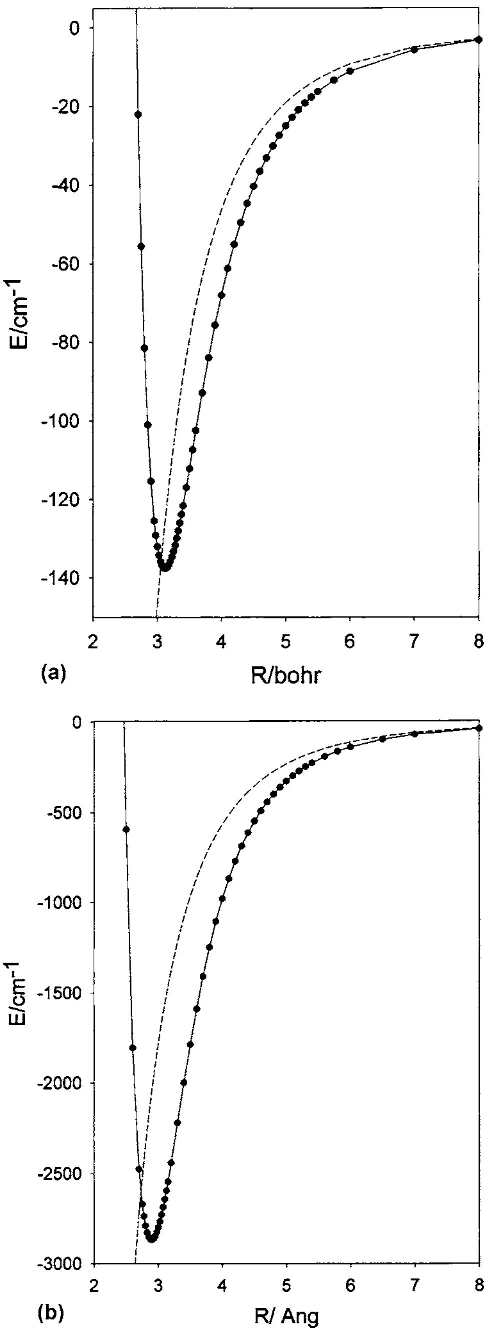

FIG. 5. Interactions potentials for (a) $Hg^{+}\cdot He$ and (b) $Hg^{+}\cdot Kr$, together with V_{pol} in each case (see text).

Note that the interatomic potential between a closed-shell metal cation and a rare-gas atom is generally expressed as the sum of a repulsion potential and the attractive dispersion and induction terms. The repulsion term is often taken, for simplicity, as a Born-Mayer potential,

$$E_{\mathrm{rep}}=Ae^{-bR}, \tag{2}$$

with the attractive induction and dispersion terms being expressed as a sum,

$$E_{\mathrm{disp,ind}}=-\sum f_n\frac{D_n}{R^r}, \tag{3}$$

where the f_n are damping factors to account for the charge overlap that occurs as the atoms approach closely. The form

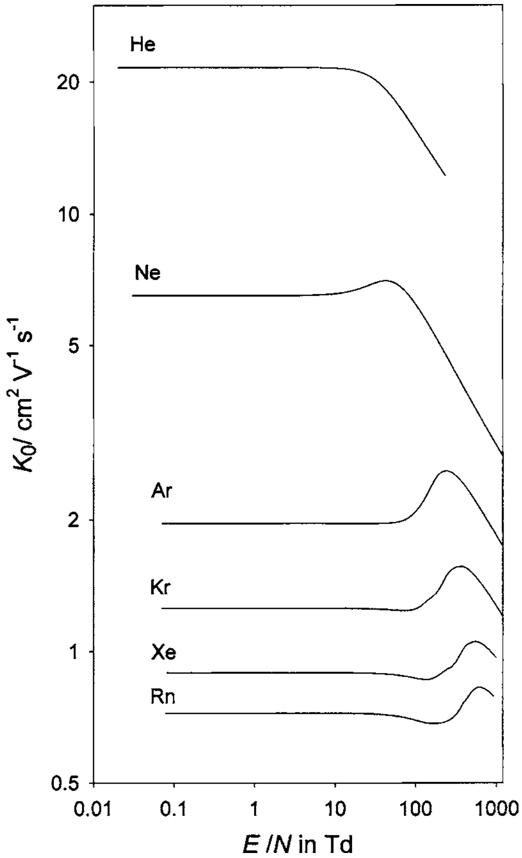

FIG. 6. Reduced mobility data for Cd^+ in Rg (log-log plot).

of the damping factors has been discussed in detail by Tang and Toennies,[47,48] Ahlrichs *et al.*,[49] and Stone,[50] with the Tang-Toennies damping factors[49] being commonly used,

$$f_n = 1 - \exp(-bR)\sum_{k=0}^{n}\frac{[bR]^k}{k!}, \tag{4}$$

(where b is generally taken as being the same exponent b obtained from a fit of the repulsive region of the curve to a Born-Mayer potential.) We tested the effect of damping functions in the present work by fitting the potential for $Hg^+ \cdot Ar$ for $R=1.0$, 1.1, and 1.2 Å, yielding $b=4.150$ Å^{-1}. For the region close to R_e, the damping function did very little to change V_{pol}, but was making more significant differences to very small R. We conclude that it makes little difference whether damping is included or not to the identification of a deviation of the potential from V_{pol}.

In Fig. 6, we show mobility data for Cd^+ in the six rare gases. Note that here, the development of the mobility minimum is less pronounced, and it is likely that this is partly due to a competition between the repulsive term (that becomes dominant at shorter values of R) and the higher-order attractive terms, of which the first is the D_6 term, which may be expressed[51,52] as

$$D_6 = \alpha_2/2 + C_6, \tag{5}$$

where α_2 is the static quadrupolar polarizability of the rare gas atom, and the C_6 term is a dispersion coefficient which depends on properties of both the rare gas and the metal atom cation. Thus, and as observed herein, the development of a mobility minimum depends on both the metal cation and the rare-gas atom, with larger systems being more prone to having mobility minima at the higher temperatures than lighter systems.

The only previous datum to which to compare our calculated mobilities is the value of 20 cm^2 V^{-1} s^{-1} (at 300 K) for Cd^+ in He[7], which is in good agreement with our values (Fig. 6).

D. The effect of isotopes on mobilities

In the case of Hg^+ and Ne, we showed that there was a very small effect upon the mobilities, whether one employs pure ^{20}Ne or a mixture of isotopes, approximating the natural abundances. In principle, in order to obtain a complete result, one should also take account of the various isotopomers of Hg^+ and Cd^+ as well, but the small percentage mass difference should mean that the effects will be very small. Such a calculation could involve a large number of transport calculations, for each pairing of rare-gas and metal ion isoto-

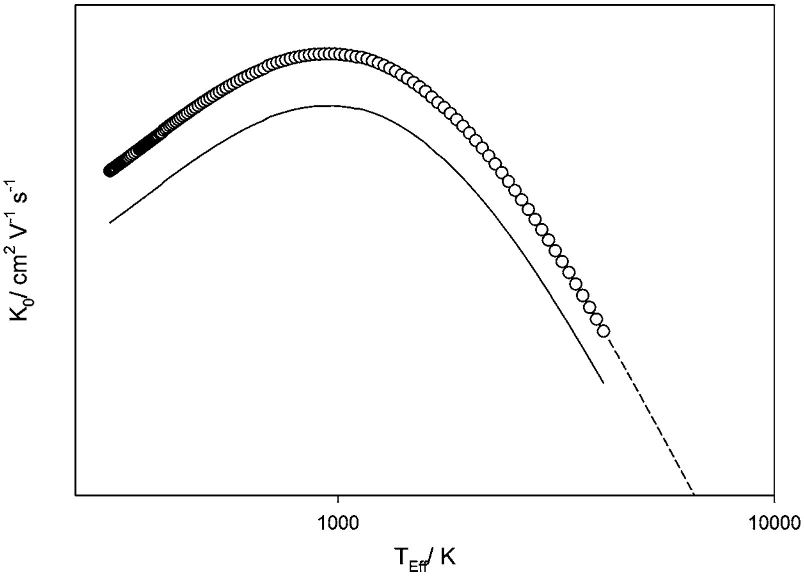

FIG. 7. Plot of reduced mobilities against the Wannier effective temperature, T_{eff}, for Hg^+ in ^{20}Ne (upper solid line) and ^{22}Ne (lower solid line). The circles are the mass-scaled ^{22}Ne mobilities, and may be seen to essentially coincide with the actual ^{20}Ne results—see text.

pomers. In fact, however, there is the possibility of employing a scaling law. Viehland and Mason[53] employed such a scaling law in studying H^+ and D^+ in Ne, and noted that the scaling was approximate, since it arose from first-order kinetic theory (see also Ref. 40). We have tested this scaling law in the present work for Hg^+, and have found it to work extremely well. We illustrate this in Fig. 7, where we have plotted the reduced ion mobility against the Wannier effective temperature T_{eff} for both pure ^{20}Ne and pure ^{22}Ne. We then scale the ^{22}Ne results to obtain the results represented by circles—these should approximate to the pure ^{20}Ne results. This is done by taking note of the following. Suppose the mobility K_1 has been measured for an ion whose isotope has molar mass m_1 and in a gas whose isotope has molar mass M_1. Similarly, suppose the mobility K_2 has been obtained for an ion with molar mass m_2 and neutral with molar mass M_2. Then the results of K_1 should be exactly the same as the results of K_2 when multiplied by

$$\left[\left(\frac{m_2}{m_1}\right)\left(\frac{M_2}{M_1}\right)\left(\frac{m_1+M_1}{m_2+M_2}\right)\right]^{1/2}, \qquad (6)$$

or equivalently,

$$K_1 = K_2\left(\frac{\mu_2}{\mu_1}\right)^{1/2}, \qquad (7)$$

where μ_i is a reduced mass. As may be seen, there is almost perfect coincidence between the scaled results and the full treatment. We therefore conclude that the mobilities of any of the isotope mixtures may be obtained from the present results by scaling the results we present herein for the combination of the most abundant isotopes.

IV. CONCLUSIONS

We report herein accurate interaction potentials for $Hg^+ \cdot Rg$ and $Cd^+ \cdot Rg$ for all six Rg atoms. In the cases where accurate rovibrational spectroscopic data exist, we obtain good agreement with previous spectroscopic data. However, it seems that previous determinations of the dissociation energy D_e are too high, probably owing to the determined ionization potentials being too low. We believe that the spectroscopic data reported herein are likely the most accurate available, except in the case of $Hg^+ \cdot Ar$, where the ultraviolet emission study of Bridge[16] is likely the more accurate, but with which we have obtained excellent agreement. The data we present for $Cd^+ \cdot Rg$ are essentially the only ones available.

With regard to mobility, the excellent agreement between the calculated and experimental data for Hg^+ in Ar is believed to be somewhat fortuitous, given the likelihood that the experimental accuracy was poorer than the cited 4%. The situation is less clear for Hg^+ in Ne, with fairly large discrepancies present between experiment and theory; this is believed to be due in part to cited error bars for the experimental measurements being too low, but there is likely another (unidentified) problem with the experimental data for this system, and we recommend that these data should be remeasured.

Of particular note is the development of a "mobility minimum" for the systems as Rg gets heavier, with the minimum being the most pronounced for Hg^+ in the heavier rare gases. This is attributable to higher-order ($>R^{-6}$) attractive terms in the interaction potential. By looking at a number of examples, including the experimental case of O^+ in Ar, for which a mobility minimum has been observed experimentally, we deduce that if V_{pol} crosses the full interaction potential at a value of R significantly smaller than R_e then a mobility minimum is likely to exist, with the magnitude of the deviation between the potential and V_{pol} being an indication of the temperatures at which the minimum will start to be manifested.

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