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Interaction potentials for He-F⁻ and Ne-F⁻

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Ab initio potential energy curves for the interaction of a fluoride anion with a He atom and a Ne atom are obtained by supermolecular CCSD(T) calculations, that is, coupled cluster calculations in the space of single and double substitutions corrected noniteratively for triple substitutions. The computations include full counterpoise corrections and employ large basis sets with bond functions. The CCSD(T) potential energy curves have significantly deeper wells than their many-body perturbation theory counterparts. Fits to functional forms that reproduce the CCSD(T) points with an average absolute error less than 0.3% are reported. © 1998 American Institute of Physics. [S0021-9606(98)30132-4]

I. INTRODUCTION

Accurate potential energy functions are now known for the van der Waals interactions among rare gas atoms,¹ between H₂ and rare gas atoms,² and between hydrogen halides and rare gas atoms.² Interactions between an ion and a rare gas atom are less well characterized particularly in the case that the ion is negatively charged. Knowledge of these ion-atom interactions is important for the understanding of processes involving the diffusion and mobility of ions in discharges, plasmas, and upper atmosphere physics.³

The interactions between halide anions and rare gas atoms have been studied by electron gas models,⁴ by ion-beam scattering measurements,^{5,6} by direct inversion of gaseous ion transport data,⁷ with an extended Tang-Toennies⁸ (ETT) model,⁹ with a universal scaling scheme¹⁰ (USS), by *ab initio* supermolecular calculations,¹¹⁻¹³ and by many-body (MB) symmetry-adapted perturbation theory^{14,15} (SAPT).

The most extensive work has been focused on He-F⁻. There is good agreement among the most recent supermolecular Møller-Plesset (MP) perturbation theory calculations¹² and MB SAPT calculations.^{14,15} However, these *ab initio* calculations are in significant disagreement with model calculations^{4,9,10} all of which differ among themselves. The situation is similar for Ne-F⁻ except that *ab initio* calculations have been restricted to a supermolecular second-order MP2 computation.¹³ The discrepancies have been traced¹⁴ to various inadequacies in the models. However, the *ab initio* calculations are not fully converged with respect to one-particle basis set effects and possibly electron correlation as well.

It is important to establish some rare gas atom-F⁻ potentials with a high degree of reliability so that methods for the inversion of mobility data and for the construction of models can be refined and calibrated. Since electron correlation and basis set effects in F⁻ can be large,¹⁶ we have performed *ab initio*, supermolecular calculations of the He-F⁻

and Ne-F⁻ interactions using high level coupled cluster methods for the incorporation of electron correlation effects and large one-particle basis sets including bond functions. Our computations show that the subtle correlation effects in He-F⁻ and Ne-F⁻ cannot be described accurately by MP theory even if it is carried through fourth-order. Our coupled cluster potential energy curves have significantly deeper wells than their MP counterparts.

Section II details our computational method and our choice of basis set. Our *ab initio* potentials are presented, compared with one another and with previous work, and fitted to compact functional forms in Sec. III. Hartree atomic units are used throughout.

II. COMPUTATIONAL METHOD

Most contemporary *ab initio* calculations of a van der Waals PES use either symmetry-adapted perturbation theory¹⁷ or the supermolecule method in which interaction energies are obtained simply as differences between the energies of the dimer and the monomers. We use the supermolecular approach.

An accurate and reliable supermolecule calculation requires adequate inclusion of electron correlation, judicious selection of the one-particle basis set, and careful control of basis set superposition error. We think there is sufficient evidence,¹⁸ both theoretical and numerical, to demonstrate that basis set superposition error can be eliminated effectively by the counterpoise method.¹⁹ We used the CCSD(T) method²⁰ to account for electron correlation effects that we expected, on the basis of previous work¹⁶ on F⁻, to be large for He-F⁻ and Ne-F⁻ interactions. The CCSD(T) method consists of the coupled cluster (CC) approximation^{21,22} with complete iterative treatment of one- and two-body clusters and a noniterative correction for the three-body clusters. In short, we compute counterpoise corrected CCSD(T) interaction energies.

The selection of the basis set of Gaussian-type functions (GTF) is crucial. Hu and Thakkar²³ showed that a combination of augmented correlation-consistent (aug-cc) basis

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sets^{24–26} with bond functions²⁷ is very effective for dispersion-dominated interactions such as those considered in this work. However, it is vital to use a large enough atom-centered substrate to ensure that the self-consistent-field (SCF) interaction energy is converged before adding bond functions.²⁷

Guided by the work of Hu and Thakkar,²³ we tested various such basis sets for the interaction energy $V(R)$ of HeF^- at an internuclear distance of $R=6.5 a_0$. The tests were carried out at the SCF and at second- and fourth-order Møller–Plesset perturbation theory (MP2, MP4) levels. We found rapid convergence and stabilization of V to about $1 \mu E_h$ using a doubly-augmented (d-aug-) cc-pVTZ basis set²⁶ combined with $\{3s3p2d1f\}$ bond functions whose exponents were taken from Tao and Pan.²⁷ $3s(\alpha=0.9,0.3,0.1)$, $3p(\alpha=0.9,0.3,0.1)$, $2d(\alpha=0.6,0.2)$, $1f(\alpha=0.3)$. This final basis set contains 123 functions made up of $[6s5p4d3f]$ and $[5s4p3d]$ contracted GTF on the F^- and He nuclei, respectively, and $\{3s3p2d1f\}$ bond functions placed halfway between F^- and He.

The basis set requirements for the Ne-F^- interaction turned out to be substantially greater. Preliminary work showed that we had to use a larger atom-centered substrate. Let A, B, and C, respectively, be the cc-pV5Z, aug-cc-pV5Z, and d-aug-cc-pV5Z basis sets^{24–26} with the g - and h -type GTF removed. We then formed five basis sets from each of A, B, and C by adding bond functions of increasing angular momentum. One such sequence of basis sets was A, $A+\{3s\}$, $A+\{3s3p\}$, $A+\{3s3p2d\}$, and $A+\{3s3p2d1f\}$. The exponents of the bond functions were the same as those listed above for He-F^- . The bond functions are placed halfway between the fluoride anion and the Ne atom. Exactly analogous sequences of basis sets were formed from B and C.

We calculated the SCF and MP2 interaction energy of Ne-F^- at $R=6 a_0$ using each of these 15 basis sets. The results are shown in Fig. 1. Observe that the SCF interaction energy is effectively converged with the B substrate. Convergence of the MP2 interaction energy takes place at $B+\{3s3p2d\}$. We chose the slightly larger $B+\{3s3p2d1f\}$ for the final calculations of the potential energy curves. This final basis set contains 183 functions made up of $[6s6p5d4f]$ contracted GTF on the F^- and Ne nuclei, and $\{3s3p2d1f\}$ bond functions placed halfway between F^- and Ne.

One and two molecular orbitals (MOs) in He-F^- and Ne-F^- , respectively, were frozen during the correlation calculations. In other words, the K -shell electrons in Ne and F^- were not correlated.

III. RESULTS AND DISCUSSION

A. Interaction energies

Tables I and II list the computed potential energy curves for He-F^- and Ne-F^- , respectively. Each of the tables lists SCF, MP2, MP3, SDQMP4, MP4, CCSD, and CCSD(T) potential energy curves. SDQMP4 means MP4 with the contributions from triple substitutions discarded but those from single (S), double (D), and quadruple (Q) substitutions and the renormalization term retained.

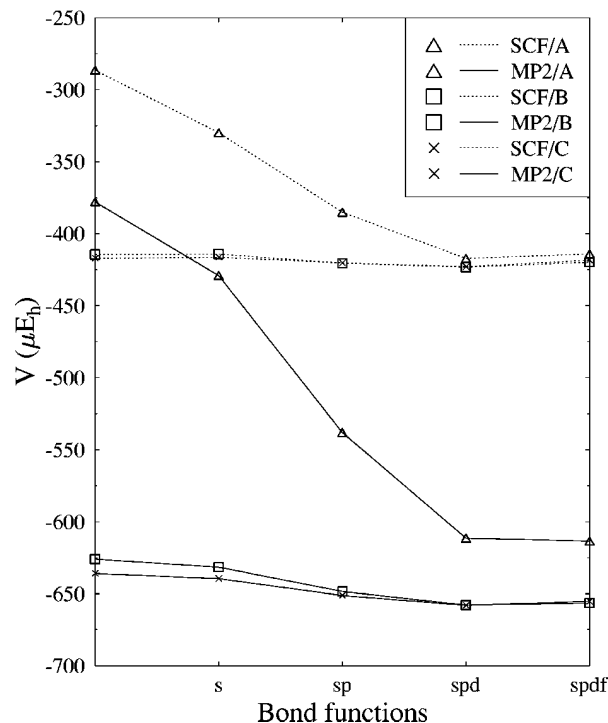


FIG. 1. Basis set variation of SCF and MP2 interaction energies for Ne-F^- at $R=6 a_0$. See text for fuller details of the basis sets.

Figure 2 displays our calculated potential energy curves for He-F^- . Comparison with the CCSD and CCSD(T) curves shows that the MP series converges very slowly in He-F^- . Observe that although the SCF, MP2, and MP4 curves are very similar in the vicinity of the minimum, they are not converged with respect to electron correlation. In the absence of the CCSD calculations, a hint that this may be so would have been provided by the substantially different MP3 curve. The clearest measure of nonconvergence of the MP series is the discrepancy between the SDQMP4 curve and its infinite-order CCSD counterpart. The difference between the CCSD and CCSD(T) curves is small showing that the triple substitutions are not very important.

As a check, we made calculations with all electrons correlated at $R=6.25 a_0$. The resulting MP2, CCSD, and CCSD(T) interaction energies of -248.75 , -346.14 , and $-335.42 \mu E_h$ are all within $0.75 \mu E_h$ of their counterparts in Table I. This demonstrates that the effects of correlating the K -shell electrons on F^- are insignificant near the minimum.

Figure 3 displays our calculated potential energy curves for Ne-F^- . Comparison with the CCSD and CCSD(T) curves shows that the MP series converges very slowly in Ne-F^- as well. The curves can be separated into three groups. The SCF curve is far too shallow. The MP2 and MP4 curves are very similar but not as deep as the CCSD, CCSD(T), and MP3 curves. Again, the difference between the CCSD and CCSD(T) curves is small showing the relative unimportance of triple substitutions.

B. Comparison with earlier work

Three parameters commonly used to characterize interaction potentials $V(R)$ are the position of zero interaction

TABLE I. Potential energy curves for He-F⁻. Distances R in a_0 and energies in μE_h .

R	SCF	MP2	MP3	SDQMP4	CCSD	MP4	CCSD(T)
4.00	5884.52	5781.24	4735.80	5296.85	5030.47	5656.92	5098.52
4.50	1917.58	1957.74	1241.41	1658.14	1448.47	1938.91	1513.22
5.00	453.60	497.06	34.02	320.04	169.63	514.42	216.39
5.25	127.14	158.04	-208.53	23.18	-101.10	179.93	-63.76
5.50	-61.10	-43.87	-331.79	-146.38	-247.73	-22.09	-218.92
5.75	-164.37	-159.36	-384.07	-237.34	-319.06	-140.21	-297.55
6.00	-215.81	-220.61	-395.06	-280.09	-345.35	-205.20	-329.86
6.25	-236.10	-248.10	-382.96	-293.72	-345.39	-236.68	-334.69
6.50	-238.07	-254.95	-358.87	-290.19	-330.81	-247.24	-323.83
6.75	-229.70	-249.50	-329.41	-276.97	-308.71	-245.02	-304.53
7.00	-215.89	-237.09	-298.44	-258.75	-283.40	-235.24	-281.27
8.00	-150.28	-168.88	-190.29	-178.32	-186.95	-172.36	-188.38
9.00	-99.51	-112.18	-120.01	-117.08	-119.99	-116.20	-121.70
10.00	-66.49	-74.50	-77.67	-77.34	-78.32	-77.65	-79.60
12.00	-32.14	-35.33	-36.14	-36.47	-36.62	-36.82	-37.15
14.00	-17.27	-18.68	-19.00	-19.20	-19.24	-19.36	-19.45

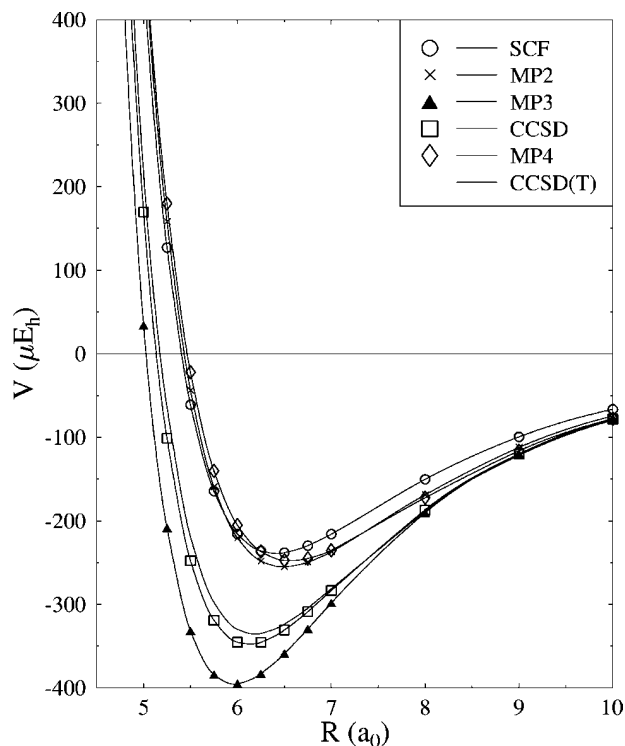
R_0 , the position of the minimum R_m , and the well depth $\epsilon = -V(R_m)$. Table III compares these parameters for He-F⁻ as predicted by our calculations at various levels with values reported in the literature. Our SCF parameters are identical with those obtained by Diercksen and Sadlej¹² using a very differently constructed, and slightly larger, basis set of $[8s4p2d]$ and $[11s9p5d3f]$ contracted GTF on He and F⁻, respectively. Our MP2, MP3, and MP4 minima R_m are within 1.3% or $0.09 a_0$, and our well depths ϵ are within 7.4% or $24\mu E_h$ of their corresponding MP values. These differences are much smaller than the differences of $0.39 a_0$ in R_m and $87\mu E_h$ in ϵ between our MP4 and CCSD(T) values. Their MP4 and our MP4 results are very similar to the MB SAPT results¹⁴ obtained with a small $[5s3p2d]$ basis set. This agreement among three calculations using very different basis sets gives us confidence that our results do not suffer from distortions produced by the bond functions. This conclusion is bolstered by the very close agreement between our CCSD(T) interaction energy of $-323.8\mu E_h$ at $R = 6.5 a_0$ and the single-point CCSD(T) value²⁸ of

$-320.0\mu E_h$. The well depths predicted by the electron gas model,⁴ the ETT model⁹ and the universal scaling model¹⁰ are 1.9, 2.4, and 1.7 times our best CCSD(T) result. Clearly, none of these models is an adequate representation of the He-F⁻ interaction.

Table IV compares potential well parameters for Ne-F⁻ as predicted by our calculations at various levels with the relatively few values reported in the literature. Our MP2 R_m and ϵ are within 1% and 4% of the corresponding MP2 values obtained by Kellö and Sadlej¹³ using a significantly smaller atom-centered basis set of $[6s5p4d3f]$ and $[7s6p4d3f]$ contracted GTF on Ne and F⁻, respectively. Our CCSD(T) results are expected to be the most accurate ones available. The well parameters predicted by the universal scaling model,¹⁰ which was handicapped by the lack of experimental ion-mobility data for this system, differ drastically from our CCSD(T) values. The potential wells predicted by the electron gas⁴ and ETT⁹ models are too deep by 59 and $159\mu E_h$, respectively.

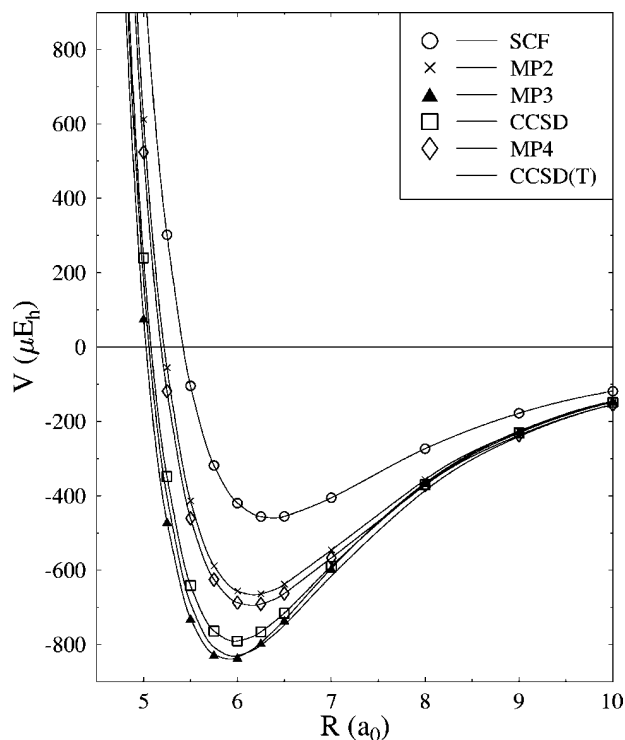
TABLE II. Potential energy curves for Ne-F⁻. Distances R in a_0 and energies in μE_h .

R	SCF	MP2	MP3	SDQMP4	CCSD	MP4	CCSD(T)
3.00	132913.96	126148.72	125449.11	125390.17	125604.88	124293.05	124644.59
4.00	14669.31	13526.20	12281.21	12995.97	12698.26	13127.49	12536.03
4.50	4511.73	3875.97	3024.10	3543.21	3297.15	3689.94	3205.92
5.00	1033.16	611.71	77.58	417.04	239.52	524.02	177.55
5.25	301.85	-56.22	-469.62	-202.69	-348.65	-118.76	-402.64
5.50	-104.37	-413.67	-729.57	-523.10	-641.06	-460.46	-689.20
5.75	-318.41	-588.26	-826.82	-669.65	-763.56	-625.36	-807.07
6.00	-419.77	-656.37	-834.53	-716.76	-790.57	-687.50	-830.11
6.25	-456.00	-663.83	-795.41	-708.61	-765.95	-691.17	-801.89
6.50	-455.53	-638.12	-734.17	-671.36	-715.44	-662.86	-748.01
7.00	-405.38	-546.08	-595.18	-564.50	-589.75	-567.15	-616.21
8.00	-273.44	-356.61	-365.87	-362.36	-369.62	-371.65	-386.28
9.00	-178.06	-227.57	-226.34	-229.27	-230.78	-237.40	-240.90
10.00	-118.85	-149.00	-145.88	-149.32	-149.23	-155.08	-155.34
12.00	-57.20	-69.60	-67.35	-69.28	-68.90	-71.87	-71.28
14.00	-30.23	-36.08	-34.81	-35.76	-35.53	-36.99	-36.58
15.00	-22.72	-26.92	-25.96	-26.65	-26.48	-27.52	-27.21

FIG. 2. Potential energy curves for He-F⁻.

C. Analytic fits

The utility of our results can be greatly enhanced by finding accurate fits of our best CCSD(T) potential energy curves to simple analytic forms. A sensible potential energy function should consist of a repulsive term and an attractive term of damped dispersion and induction energies. After

FIG. 3. Potential energy curves for Ne-F⁻.TABLE III. Positions of the energy zero R_0 and minimum R_m , and well depths ϵ for He-F⁻.

Method	R_0/a_0	R_m/a_0	$\epsilon/(\mu E_h)$
SCF ^a	5.40	6.41	239
MP2 ^a	5.43	6.49	255
MP3 ^a	5.03	5.97	395
SDQMP4 ^a	5.28	6.31	294
CCSD ^a	5.14	6.12	348
MP4 ^a	5.46	6.57	248
CCSD(T) ^a	5.18	6.18	335
Mobilities ^b	>4.6		
ETT ^c	4.70	5.47	790
EG III ^d	4.80	5.65	650
USS ^e		5.63	563
MP4 ^f	5.4	6.5	290
SCF ^g	5.40	6.41	238
MP2 ^g	5.50	6.57	241
MP3 ^g	5.19	6.05	371
MP4 ^g	5.56	6.66	231
MB SAPT ^h	5.59	6.65	255

^a*Ab initio* supermolecule calculations, this work.

^bInversion of experimental data, Ref. 7.

^cExtended Tang-Toennies semi-empirical model, Ref. 9.

^dElectron gas model, Ref. 4.

^eEmpirical universal scaling scheme, Ref. 10.

^f*Ab initio* supermolecule calculations, Ref. 11.

^g*Ab initio* supermolecule calculations, Ref. 12.

^h*Ab initio* many-body symmetry-adapted perturbation theory, Ref. 14.

some trial and error, we found that it was most efficient to represent the repulsive term by a Born-Mayer form with a R -dependent range parameter. The potential energy function we use is given by

$$V(R) = A \exp(-b(R)) - \sum_{n=2}^5 \frac{C_{2n} g_{2n}(\rho R)}{R^{2n}}, \quad (1)$$

in which

$$b(R) = (b_0 + b_1 z + b_2 z^2)R, \quad (2)$$

with

$$z = \frac{R - R_s}{R + R_s}. \quad (3)$$

TABLE IV. Positions of the energy zero R_0 and minimum R_m , and well depths ϵ for Ne-F⁻.

Method	R_0/a_0	R_m/a_0	$\epsilon/(\mu E_h)$
SCF ^a	5.42	6.36	459
MP2 ^a	5.22	6.16	666
MP3 ^a	5.03	5.90	839
SDQMP4 ^a	5.15	6.07	719
CCSD ^a	5.08	5.98	791
MP4 ^a	5.19	6.14	695
CCSD(T) ^a	5.06	5.96	831
EG III ^b	5.18	6.05	890
ETT ^c	5.07	5.92	990
USS ^d		4.61	2790
MP2 ^e	5.35	6.10	640

^a*Ab initio* supermolecule calculations, this work.

^bElectron gas model, Ref. 4.

^cExtended Tang-Toennies semi-empirical model, Ref. 9.

^dEmpirical universal scaling scheme, Ref. 10.

^e*Ab initio* supermolecule calculations, Ref. 13.

TABLE V. Potential energy function fit parameters in atomic units.

Parameter	He-F ⁻	Ne-F ⁻
A	131.1	29.24
b ₀	2.303 27	1.804
b ₁	-1.1302	-0.678
b ₂	0.516	-2.128
R _s	5.357	6.013
ρ	0.6033	0.760 85
C ₄	0.6834	1.35
C ₆	8.388	20.56
C ₈	185	353
C ₁₀	109 350	73 000

The C_{2n} are combined dispersion and induction coefficients, and the $g_{2n}(R)$ are damping functions of the form introduced by Douketis *et al.*:²⁹

$$g_n(\rho R) = [1 - \exp(-2.1\rho R/n - 0.109\rho^2 R^2/\sqrt{n})]^n. \quad (4)$$

This function has five parameters in the repulsive part (A, b_0, b_1, b_2, R_s) and five in the attractive part ($\rho, C_4, C_6, C_8, C_{10}$). The C_4 coefficient is entirely inductive and can be expressed as $C_4 = \alpha_1(A)/2$ in which $\alpha_1(A)$ is the static dipole polarizability of the rare gas atom A . We considered fixing the C_4 coefficient using the well-established polarizabilities^{30,31} $\alpha_1 = 1.3832$ and $\alpha_1 = 2.70$ for He and Ne, respectively. However, one really ought to fix the C_4 coefficients using dipole polarizabilities computed with the same basis sets as those used for the interaction energy calculations. Instead, we found it most convenient to obtain all ten parameters by minimizing the mean absolute percent error of the fit subject to the constraint that C_4 vary within a very small interval about its exact value.

The parameters of the fits to our CCSD(T) potential energy curves are listed in Table V. They have been rounded to the minimum number of significant figures required to maintain the accuracy of the fits. These compact representations of the CCSD(T) curves have an average absolute percent deviation of 0.08% and 0.27% for He-F⁻ and Ne-F⁻, respectively.

Observe that the C_4 coefficients are very close to their theoretical values. The fitted C_6 coefficients, 8.39 and 20.6 for He-F⁻ and Ne-F⁻, respectively, are reasonably close to their asymptotic values—9.05 and 19.5 as estimated by Ahlrichs *et al.*,⁹ and 8.66 and 18.2 as estimated by Koutselos and co-workers.¹⁰ Similarly the fitted C_8 coefficients, 185 and 353 for He-F⁻ and Ne-F⁻, respectively, are close to the values of 170 and 373 estimated by Ahlrichs and co-workers,⁹ and to 158 and 367 as estimated by Koutselos *et al.*¹⁰ However, the fitted values of C_{10} , 1.1×10^5 and 7.3×10^4 for He-F⁻ and Ne-F⁻, respectively, are much larger than the estimated values⁹ of 4.5×10^3 and 9.9×10^3 . Presumably this is because the R^{-10} term compensates for the omission of higher-order terms.

IV. CONCLUDING REMARKS

Our CCSD(T) potential energy curves are likely to be the most accurate ones currently available for He-F⁻ and

Ne-F⁻. It is hard to assess their accuracy but we would be surprised if they were to differ from the true curves by more than 10% over the range of internuclear distances sampled in this work. Our analytic fits facilitate the computation of physical properties from the potential energy functions. A FORTRAN subroutine to evaluate these fitted functions is available by anonymous ftp from `ftp://okapi.chem.unb.ca/pub/imf/fmrg/vccsdt.for`.

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