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Coupled-electron-pair approximation calculations on open-shell molecules: The two lowest states of $HeNe^+$

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Extensive *ab initio* calculations at coupled-electron-pair approximation and multireference configuration interaction levels have been performed for the two lowest states $X\,^2\Sigma^+$ and $A\,^2\Pi$ of $HeNe^+$. Spin-orbit coupling has been included on a semiempirical basis in order to account for the strong mixing between the $X\,^2\Sigma^+_{1/2}$ and $A_2\,^2\Pi_{1/2}$ components, which influences the properties of both these states in the experimentally observed region at large internuclear distances. After a careful analysis of electron-correlation effects in the X state, we were able to interpret the observed spectrum of $HeNe^+$ and to explain the large discrepancies between experiment and previous *ab initio* calculations. We conclude that the determination of the equilibrium properties such as R_e, ω_e, etc. from the observed vibrational intervals and rotational constants of high vibrational levels has led to incorrect "experimental" values for the $X\,^2\Sigma^+_{1/2}$ ground state. Our predictions for $^4HeNe^+$ are [in cm^{-1}, experimental results from Dabrowski and Herzberg, J. Mol. Spectrosc. **73**, 183 (1978) in parentheses] (i) $X\,^2\Sigma^+_{1/2}$ state: $R_e=1.43$ (1.300) Å, $D_e=5492$ (6216±300), $\omega_e=913$ (1308); the vibrational intervals $\Delta G(v+\frac{1}{2})$ are 349 (341.59), 229 (233.42), 135 (146.27), and the corresponding rotational constants B_v are 1.610 (1.58983), 1.361 (1.35755), 1.083 (1.09037), 0.814 (0.8431) for $v=6,7,8,9$, respectively; (ii) $A_2\,^2\Pi_{1/2}$ state: $R_e=2.36$ (2.318) Å, $D_e=328$ (347.2), $\Delta G(\frac{1}{2})=119$ (129.69), $B_0=0.840$ (0.86571), $B_1=0.674$ (0.71658). Two more vibrational levels should exist for this state, as is also suggested recently by another experiment and by semiempirical model calculations. Results of similar quality were obtained also for $^3HeNe^+$. The calculated properties of the experimentally unobserved $A_1\,^2\Pi_{3/2}$ state differ very much from those of the $A_2\,^2\Pi_{1/2}$ component of the same $A\,^2\Pi$ state.

I. INTRODUCTION

The electronic spectrum of $HeNe^+$ consists of two band groups near 4250 and 4100 Å. These bands were first observed by Druyvesteyn,[1] but have been assigned to $HeNe^+$ by Tanaka, Yoshino, and Freeman.[2] Dabrowski and Herzberg[3] have analyzed these two band groups in high resolution for both $^4HeNe^+$ and $^3HeNe^+$ and have obtained vibration frequencies, rotational constants, and dissociation energies for the electronic states involved. More recently, the vibration-rotation levels belonging to the two lowest electronic states of $^4HeNe^+$ have been analyzed by Carrington and Softley[4] using the technique of infrared predissociation spectroscopy. At the same time, Hausamann and Morgner,[5] using a large set of experimental data and a simple semiempirical model for interactions between noble-gas atoms and their ions, determined the essential features of the potential curves of heteronuclear rare-gas ions, among them $HeNe^+$.

The analysis of Dabrowski and Herzberg[3] shows some inconsistencies which will be discussed in Sec. II. Furthermore, there is considerable disagreement between the experimental molecular constants proposed by these authors and the results of all theoretical calculations on $HeNe^+$ reported so far in the literature. Since there is rather large experimental interest in the excited states of $HeNe^+$ (Refs. 6 and 7), and since none of the previous calculations on $HeNe^+$ seems to be very accurate, we have performed a series of *ab initio* calculations using rather large basis sets and sophisticated methods in order to clarify the discrepancy between experiment and the earlier calculations.

II. DISCUSSION OF PREVIOUS WORK

$HeNe^+$ has three low-lying electronic states. The highest of them (B state) represents a weak interaction between $He^+(^2S_{1/2})$ and $Ne(^1S_0)$ and has the spectroscopic designation $B\,^2\Sigma^+_{1/2}$. The other two states correspond to the interaction between $He(^1S_0)$ and $Ne^+(^2P)$ and are expected to lie about 24 000 cm^{-1} below the B state, since the difference between the lowest ionization potentials of He and Ne amounts to 24 373 cm^{-1}.[8]

The ^2P ground state of Ne^+ is split by spin-orbit interaction into two components, $^2P_{3/2}$ and $^2P_{1/2}$, the $^2P_{3/2}$ state being the lower of the two (inverted multiplet); the observed fine-structure splitting in the isolated Ne^+ ion is 780.34 cm^{-1}.[9,10] However, in $HeNe^+$, i.e., in $C_{\infty v}$ symmetry, the ^2P ground state of Ne^+ is split into a $^2\Sigma^+$ and a $^2\Pi$ state; the first of them gives rise to the $X\,^2\Sigma^+_{1/2}$ ground state of $HeNe^+$ and correlates with the $M_J=\frac{1}{2}$ component of the $^2P_{3/2}$ state of isolated Ne^+, while the $^2\Pi$ state is split by the spin-orbit interaction into a (lower) $A_1\,^2\Pi_{3/2}$ component correlating with the $M_J=\frac{3}{2}$ component of $^2P_{3/2}$ and a (higher) $A_2\,^2\Pi_{1/2}$ component correlating with $^2P_{1/2}$ of isolated Ne$^+$.

According to the analysis of Dabrowski and Herzberg[3] the band group at 4250 Å is assigned to the charge transfer transition $B\,^2\Sigma^+_{1/2} \rightarrow A_2\,^2\Pi_{1/2}$, the band group at 4100 Å to $B\,^2\Sigma^+_{1/2} \rightarrow X\,^2\Sigma^+_{1/2}$, while the transition $B\,^2\Sigma^+_{1/2} \rightarrow A_1\,^2\Pi_{3/2}$ has not been observed. These assignments have been confirmed by more recent investigations of radiative charge transfer by Johnsen[11] as well as by the analysis of Ref. 4. The $X\,^2\Sigma^+_{1/2}$ ground state was found to be moderately strongly bound [$D_e = 6216 \pm 300$ cm$^{-1} \cong 0.77$ eV for ^{4}HeNe$^+$ (Ref. 3)], while the two higher states exhibit only very shallow minima:[3] $D_e = 364$ cm^{-1} for $B\,^2\Sigma^+_{1/2}$ and $D_e = 347$ cm^{-1} for $A_2\,^2\Pi_{1/2}$. The results of the semiempirical model of Hausamann and Morgner[5] are consistent with these experimental findings.

The results of the spectroscopic analysis[3] of the two band systems show the following inconsistencies.

(1) The R_e values for the $X\,^2\Sigma^+$ state differ for ^{4}HeNe$^+$ (1.300 Å) and ^{3}HeNe$^+$ (1.330 Å) by as much as 0.030 Å. This is a consequence of the extrapolations from the observed rotational constants B_v with $v = 6,7,8,9$ down to $v = 0$. A difference of 0.030 Å in the equilibrium distances of two isotopic species seems to be much too large for a molecule with a rather deep, not strongly anharmonic potential. There is no indication that the Born-Oppenheimer approximation is violated, since the separation between the X-state potential curve at its minimum and all the other electronic states is large and no curve crossing exists in this region.

(2) Using the results given in Table XII of Ref. 3 for ω_e, $\omega_e x_e$, and $\omega_e y_e$ for the X state of ^{4}HeNe$^+$, we were not able to reproduce the observed vibrational intervals. We calculated 342.0,239.9,146.8 cm^{-1} for $\Delta G(v + \frac{1}{2})$, $v = 6,7,8$, instead of the observed values 341.6,233.4,146.3 cm^{-1}, respectively. For ^{3}HeNe$^+$ there is the same discrepancy of 6.5 cm^{-1} in the second ΔG value.

(3) For the A_2 state only one vibrational interval has been observed, both for ^{4}HeNe$^+$ and ^{3}HeNe$^+$. Dabrowski and Herzberg[3] concluded that there are only two bound vibrational levels with $v = 0,1$; hence the potential has to rise rather steeply from the minimum to its asymptotic value. On the other hand, the long-range part of the A_2 potential should behave like $-\frac{1}{2}\alpha_{\mathrm{He}} R^{-4}$, α_{He} being the polarizability of He. Such a long-range potential would certainly contain more than two vibrational levels and would look quite different from the Rydberg-Klein-Rees (RKR) potential given in Fig. 8 of Ref. 3. A more realistic picture of the A_2 potential curve is presented in Fig. 1 of Ref. 4, where the long-range R^{-4} behavior was used for approximating the potential. Carrington and Softley[4] suggest the existence of at least two more vibrational levels ($v = 2,3$), which would be responsible for many lines unresolved in their study. The existence of vibrational levels up to $v = 3$ is predicted also from the semiempirical potential of Hausamann and Morgner.[5]

For the B state a short progression of vibrational intervals has been observed; the expected R^{-4} behavior has been confirmed and has actually been used to calculate the D_e value.[3]

There are also several *ab initio* calculations of the HeNe$^+$ potential-energy curves,[12–16] mainly performed in order to interpret the inelastic scattering of He$^+$ ions by Ne atoms (Refs. 17–21 and many others). The early calculations[12–14] focused on the crossing between the B state and higher electronically excited states at very high energies and small internuclear separations. The calculation by Barat *et al.*[14] places the minimum of the X state at 1.46 Å with a depth of 1.3 eV. Later, Blint[15] and Kendrick and Kuntz[16] tried to obtain reasonably accurate potential curves for the three lowest states of HeNe$^+$. But these results are in considerable disagreement with the spectroscopic analysis:[3] Using a configuration interaction (CI) with a medium-sized basis set and about 1000 configurations Blint[15] got a minimum at 1.49 Å with $D_e = 0.6$ eV for the ground state and no minimum at all for the A state. Kendrick and Kuntz[16] obtained results of similar quality from a valence-bond calculation: $D_e = 0.747$ eV at $R_e = 1.473$ Å with a minimal basis, $D_e = 0.708$ eV at $R_e = 1.485$ Å with an extended basis, both for the $X\,^2\Sigma^+$ state. More recently, Cooper *et al.*[22] performed calculations with an extended basis set and a multireference configuration interaction (MRCI)-type wave function with about 13 000 configurations, but did not publish their potential curves; their paper is mainly concerned with transition probabilities in the He$^+$-Ne collision system. Finally, unpublished complete active space self-consistent field (CASSCF) and externally contracted CI (CCI) calculations with large basis sets performed by Hotokka[23] yielded $D_e = 0.5$ eV at $R_e = 1.46$ Å for the $X\,^2\Sigma$ state.

Though quantum-chemical *ab initio* calculations can easily be charged with errors of 0.1 to 0.2 eV in the calculated binding energy, the discrepancy between the observed and calculated R_e values is extraordinarily large for a system with a moderately deep potential. It is even more surprising that several calculations using completely different methods end up with practically the same result for R_e which differs by 0.15 Å from experiment. We believe that the main reason for this discrepancy is that the "experimental" equilibrium properties R_e, ω_e, D_e of the ground state have been determined by extrapolation of observed ΔG and B_v values from rather high vibrational levels down to $v = 0$. Unfortunately, due to the Franck-Condon principle, only high vibrational levels of the ground state can be observed spectroscopically,[3,4] and no direct information on the lower vibrational levels is available.

III. BASIS SETS AND METHOD OF CALCULATION

The basis sets used in the present calculations consisted of contracted Gaussian lobe functions with exponents given by Huzinaga.[24,25] We started either from a $9s5p$ set for Ne and a $6s$ set for He (basis sets X-34,X-50,A-56,A-67, cf. Table I) or from a $11s7p$ set on Ne and an $8s$ set for He (basis X-72). All these basis sets had to be augmented by additional diffuse functions and polarization functions. The diffuse functions were particularly important for the A state because of its very shallow minimum (diffuse p on He), while higher angular terms are needed to account for electron-correlation effects which are re-

TABLE I. Basis sets for $HeNe^+$.

State	Designation (size Ne,He)	Atom	Standard set[a]	Contraction[b]	Additional functions and exponents
$X\,^2\Sigma^+$	X-34	Ne	$9s5p$	$5,4\times1;3,2\times1$	d: 2.15,0.6
	(24,10)	He	$6s$	$3,3\times1$	p: 2.5,0.7
	X-50	Ne	$9s5p$	$5,4\times1;2,3\times1$	s: 0.14
	(36,14)				p: 0.097
					d: 4.5,1.3,0.4
		He	$6s$	as X-34	s: 0.059
					p: 2.5,0.7,0.2
	X-72	Ne	$11s7p$	$5,6\times1;3,4\times1$	s: 0.11
	(48,24)				p: 0.081
					d: as X-50
					f: 2.8
		He	$8s$	$3,5\times1$	s: 0.048
					p: as X-50 + 0.058
					d: 0.5
$A\,^2\Pi$	A-56	Ne	$9s5p$	as X-34	as X-50[c]
	(31,25)	He	$6s$	as X-34	s: as X-50
					p: as X-50 + 0.055
					d: 0.5,0.15[c]
	A-67	Ne	$9s5p$	as X-34	s: 0.14,0.045
	(37,30)				p: 0.097,0.03
					d: as X-50
		He	$6s$	as X-34	s: as X-50
					p: as A-56 + 0.02
					d: 0.5,0.15

[a] Basis sets from Huzinaga, Ref. 24 for He, Ref. 25 for Ne.

[b] $5,4\times1$ means the following: the five functions with the highest exponents contracted to one group, the four remaining functions uncontracted.

[c] $d\delta$ components for the d set with the lowest exponent omitted.

sponsible for the bonding in the ground state. The five basis sets with which most of our calculations have been performed are presented in Table I, but in the course of choosing adequate basis sets we have explored many more.

It should be mentioned that we encountered considerable difficulties in the convergence of the self-consistent-field (SCF) calculations for the X state at distances $R \geq 4.0a_0$. The reason has been a mismatch between the energetic order of the orbitals and the electronic states: For larger interatomic distances the orbital energy of the doubly occupied $1s$ orbital of He is higher than that of the singly occupied $2p\sigma$ orbital of Ne^+; since they have the same symmetry they are rotated into each other and the $2p\sigma$ orbital will eventually become doubly occupied, leading to the $B\,^2\Sigma^+$ state. This difficulty was circumvented by a level shift technique. For the A state the SCF calculations were spin restricted (i.e., yielding pure doublets), but spatially unrestricted; the singly and the doubly occupied π orbitals were not forced to have the same radial parts.

The correlation energy has been calculated primarily by using the open-shell coupled-electron-pair approximation (CEPA) program written in Bochum and described in detail in Ref. 26. For details we refer to this paper and mention only some technical points. The threshold for the truncation of the pair natural orbital (PNO) expansion was 10^{-6} a.u. $=1$ μhartree throughout; the $1s$ electrons of Ne were not included in the correlation treatment; we have used the CEPA-2 variant[26–28] starting from canonical SCF orbitals. Inclusion of singly excited configurations was compulsory in most cases; we use the notation (SD) and (D) to distinguish between the calculations with and without singles, respectively, for both the CEPA and CI approaches.

In the following we will only discuss interaction energies. They are reported relative to the total energies of the isolated systems as given in Table II for the SCF and CEPA approximations.

The CEPA(SD) approach was fully satisfying and internally consistent for the $A\,^2\Pi$ state, but not at all so for the $X\,^2\Sigma^+$ ground state. Therefore we have performed additional calculations using the MRCI(SD) approach for this state. We applied the code of Ahlrichs *et al.*,[29] which is basically a Cyber 205 vectorized version of the HONDO program[30] combined with the Columbus program system.[31]

In order to demonstrate the computational problems connected with the $X\,^2\Sigma^+$ state, we have collected in Table III the interaction energies $V(R)$, obtained in various approximations for two characteristic distances: $R=2.8a_0$ (close to the equilibrium distance of the X state) and $R=5.0a_0$ (close to the minimum in the B state). These distances have been chosen to show how strongly the errors affect the dissociation energy D_e and the transition energy T_e for the observed emission $B \rightarrow X$ (4100-Å band). One first observes that the interaction energies depend little on the basis set used; the differences between the small basis X-34 (used only for introductory investigations) and the final extended basis X-72 is small compared to the differences between the various approaches, in particular in the region of the minimum ($R = 2.8a_0$). Therefore we believe that the problems with the X state are not due to too small basis sets and that the basis X-72 can be considered as sufficiently large (cf. also Ref. 23).

As will be shown in Sec. V (Table IV), the SCF approximation yields a minimum for the X state which is much too shallow and occurs at much too large R. It is primarily an inductive minimum (polarization of He by the positive charge on Ne^+), and it is very similar to the minimum of the A state. However, in the X state, electron-correlation effects give rise to a chemical bond at a much smaller distance than the inductive minimum.

The results in Table III show that all four "single-reference" treatments of electron-correlation effects [CI(D), CI(SD), CEPA(D), CEPA(SD)] lower the X-state potential curve at small distances considerably, thus leading to pronounced minima between $2.7a_0$ and $2.8a_0$. However, there are unusually large differences between these four treatments, as follows.

(1) The CI potential curves are much too shallow around $R = 2.8a_0$. In addition, because of the nonseparability of the CI treatment starting from the single-reference determinant

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^4 4\sigma \tag{1}$$

(leading configuration in the CI expansion of the X state), they are asymptotically incorrect as can be seen from the positive values of the interaction energy at $R = 5.0a_0$.

(2) The CI and CEPA interaction energies differ by as much as nearly a factor of 2 at $R = 2.8a_0$.

(3) Single excitations do not contribute to the correlation energy in second-order perturbation theory, since the Brillouin theorem holds for configuration (1). For small and large distances (e.g., $R = 5.0a_0$ in Table III) the influence of the singles is indeed rather small. But at intermediate distances ($2.5 < R < 4.0a_0$) there is a large increase of the correlation energy upon inclusion of singles, in particular in the CEPA.

TABLE II. Asymptotic values of SCF energies and CEPA(SD) correlation energies calculated using different basis sets and compared with the corresponding accurate values. All entries are in hartrees.

	Basis[a] set	He	Ne^+
SCF	X-34	−2.861 116	−127.795 970
	X-50	−2.861 129	−127.796 667
	X-72	−2.861 610	−127.817 067
	A-56	-2.861 129	−127.796 636
	A-67	−2.861 129	−127.797 044
	accurate	−2.861 680[b]	−127.817 831[c]
CEPA(SD)	X-34	−0.037 706	−0.180 180
	X-50	−0.037 756	−0.199 128
	X-72	−0.038 288	−0.223 909
	A-56	−0.038 139	−0.193 526
	A-67	−0.038 152	−0.194 095
	accurate	−0.042 027[d]	−0.2626±0.001[e]

[a] Compare Table I.
[b] Reference 36.
[c] SCF calculations of the present authors.
[d] Reference 37.
[e] Reference 38, method described in Ref. 39.

Responsible for the large influence of the singles at intermediate distances and for the large differences between CEPA and CI potential curves is the contribution of a certain class of triple excitations. In particular, those triples are important which are doubly excited with respect to the leading configuration of the $B\,^2\Sigma^+$ state,

$$1\sigma^2 2\sigma^2 3\sigma 1\pi^4 4\sigma^2 \ . \tag{2}$$

They are not at all included in the CI(D) and CEPA(D) treatments and are only estimated as "unlinked clusters of singles and doubles" in the CEPA(SD) method.[26] If the coupling between the X and $B\,^2\Sigma^+$ states increases exponentially with decreasing R (as it is assumed, e.g., in the model used by Hausamann and Morgner[5]), then there should be a region of large interaction before the energy

TABLE III. Interaction energies $E(R) - E(\infty)$ for the $X\,^2\Sigma^+$ state calculated using different methods and basis sets for two selected interatomic distances R. All entries are in mhartrees.

	Basis sets[a] and values of R (a_0)					
	X-34		X-50		X-72	
Method	2.8	5.0	2.8	5.0	2.8	5.0
SCF	+4.197	−0.712	+4.096	−1.317	+4.520	−1.249
CI(D)	−7.979	+1.353	−8.110	+0.878	−7.720	+1.162
CI(SD)	−12.583	+1.334	−12.460	+0.855	−11.993	+1.140
CEPA(D)	−11.750	−0.881	−12.227	−1.568	−12.240	−1.535
CEPA(SD)	−21.098	−1.002	−21.712	−1.712	−22.022	−1.669
MRCI(SD)	−21.710	−0.945			−22.873	−1.489
MRCI(SD)-DC	−23.574	−0.960			−25.055	−1.507
MRCI(SD)-EDC	−24.301	−0.968			−25.612	−1.513

[a] Compare Table I.

separation between the two states becomes too large at small distances.

In order to account for these triple excitations we performed MRCI(SD) calculations starting from the two reference determinants (1) and (2). Since they are singly excited relative to each other, a two-configuration multiconfiguration self-consistent field (MCSCF) including (1) and (2) is not possible. Instead of using a CASSCF with a larger active space (cf. Ref. 23) we started from the SCF orbitals of the ${}^1\Sigma^+$ ground state of neutral HeNe, which represents a balanced description of the two orbitals 3σ and 4σ.

The MRCI(SD) wave function starting from the two references (1) and (2) is still not size consistent. Though it contains the most important triples explicitly, other unlinked cluster contributions, e.g., unlinked clusters of doubles, are still missing. We have estimated their effect by using the widely known Davidson correction[32] (DC) technique. The scaling was applied to the "correlation energy" defined formally as the difference between the MRCI(SD) total energy and the SCF energy [single-configuration SCF energy for the determinant (1)],

$$E_{\mathrm{corr}}^{\mathrm{MRCI(SD)-DC}} \equiv f(R)[E_{\mathrm{MRCI(SD)}}(R) - E_{\mathrm{SCF}}(R)] \; , \tag{3}$$

with the scaling factor defined, as usual, as

$$f(R) = 1/C_X^2(R) \; , \tag{4}$$

$C_X(R)$ being the MRCI expansion coefficient of the leading configuration (1) in the MRCI(SD) wave function of the X state. When this approach is applied to the interaction energy, one obtains the following formula:

$$V_{\mathrm{MRCI(SD)-DC}}(R) = f(R)V_{\mathrm{MRCI(SD)}}(R) + [1 - f(R)]V_{\mathrm{SCF}}(R) + [f(R) - f(\infty)][E_{\mathrm{MRCI(SD)}}(\infty) - E_{\mathrm{SCF}}(\infty)] \; . \tag{5}$$

The scaling function $f(R)$ (4) for our calculations varies with R only very slightly (in the range 1.08–1.12). In the last term of (5) the asymptotic value of our correlation energy is multiplied by the difference of scaling factors, which is a very small quantity. For this reason we decided to omit this term, in order to avoid possible numerical artifacts. Moreover, since the $C_X(R)$ coefficients are not exactly those which would appear in the MRCI expansion based on orbitals optimized in the single-configuration SCF calculations for the ion, we consider it a reasonable approximation also to use a constant scaling factor f instead of the function (4). This is consistent with omitting the last term in (5). The choice of the optimum f value can be based on some empirical criteria; for this reason this approximation will be referred to as the "empirical" Davidson correction (EDC).

The values of the interaction energies calculated with the three MRCI(SD) approaches are also included in Table III. Obviously, CEPA(SD) and MRCI(SD) are rather similar, but the Davidson correction on top of MRCI(SD) lowers the well depth by about 2 mhartree. For the EDC curve, we have chosen the constant value $f = 1.10$, since (i) it is in the middle of the range of $1/C_X^2$ values and (ii) it reproduces the experimental ΔG values for $v = 6, 7, 8$.

IV. SPIN-ORBIT INTERACTION

The spin-orbit coupling, resulting in the fine-structure splitting of the asymptotic states of Ne$^+$, ${}^2P_{1/2}$, and ${}^2P_{3/2}$, must also be included in the molecular calculations. Otherwise the calculated vibrational intervals and rotational constants have errors so large that they cannot be compared with the corresponding experimental values. The spin-orbit interaction influences, in particular, those regions of the X and A potential curves, which are involved in the observed emission from the $B\,{}^2\Sigma^+$ state, as can be seen in Fig. 8 of Ref. 3 or Fig. 1 of Ref. 4.

We have applied a semiempirical treatment of the spin-orbit coupling (SOC) as described, e.g., in Ref. 33 for HeAr$^+$. The interaction of the two $\Omega = \frac{1}{2}$ states, i.e., $X\,{}^2\Sigma_{1/2}^+$ and $A_2\,{}^2\Pi_{1/2}$, due to SOC is described by a perturbation operator $H_{\mathrm{s.o.}}$ that contains an R-independent spin-orbit coupling constant ζ and reproduces the fine-structure splitting of Ne$^+$ for $R \rightarrow \infty$,

$$\begin{aligned}\langle LSJ \mid H_{\mathrm{s.o.}} \mid LSJ \rangle &= E_{\mathrm{s.o.}}^{(1)}(LSJ) \\ &= \zeta(LS) \\ &\quad \times \frac{J(J+1) - L(L+1) - S(S+1)}{2} \; .\end{aligned} \tag{6}$$

For Ne$^+$, ${}^2P$, we have[9,10]

$$E({}^2P_{1/2}) - E({}^2P_{3/2}) = -\tfrac{3}{2}\zeta({}^2P) = 780.34 \text{ cm}^{-1} \tag{7}$$

or

$$\zeta = -520.23 \text{ cm}^{-1} = -2.370 \text{ mhartree} \; . \tag{8}$$

After evaluating the necessary matrix elements the energies of the two $\Omega = \frac{1}{2}$ states at finite separation R are given by

$$\begin{aligned}\varepsilon_{1,2}(R) &= \tfrac{1}{2}(E_X + E_A) - \tfrac{1}{4}\zeta \\ &\quad \pm \tfrac{1}{2}[\tfrac{9}{4}\zeta^2 + \zeta(E_X - E_A) + (E_X - E_A)^2]^{1/2} \; ,\end{aligned} \tag{9}$$

where E_X and E_A are the R-dependent nonrelativistic energies of the $X\,{}^2\Sigma^+$ and $A\,{}^2\Pi$ states. The energy of the $\Omega = \frac{3}{2}$ state is only shifted by $\frac{1}{2}\zeta$,

$$E_{A_1}^{\mathrm{SOC}}(R) \equiv \varepsilon_3(R) = E_A + \tfrac{1}{2}\zeta \; . \tag{10}$$

In accordance with first-order perturbation theory the weighted mean of the fine-structure levels is identical with the nonrelativistic energy; in the corresponding formulas of Ref. 33 a slightly different choice has been made.

For $\zeta \ll |E_X - E_A|$ (small distances) the energies $\varepsilon_{1,2}$ have the form

$$E_X^{\mathrm{SOC}}(R) \equiv \varepsilon_1(R) \cong E_X - \frac{1}{2}\frac{\zeta^2}{|E_X - E_A|}\ , \tag{11}$$

$$E_{A_2}^{\mathrm{SOC}}(R) \equiv \varepsilon_2(R) \cong E_A - \frac{\zeta}{2} + \frac{1}{2}\frac{\zeta^2}{|E_X - E_A|}\ . \tag{12}$$

This means that ε_1 becomes identical to E_X for small R ($R \le 3.0a_0$), i.e., that the minimum of the ground state is practically not affected by SOC. For large R, however, ε_1 is lower than E_X. This leads to large changes in the vibrational intervals for those higher vibrational levels which have been observed experimentally.[3,4] When the difference $|E_X - E_A|$ increases (for $R \to 0$) the splitting of the two ($A\ ^2\Pi$)-state components,

$$\varepsilon_2 - \varepsilon_3 \equiv E_{A_2}^{\mathrm{SOC}} - E_{A_1}^{\mathrm{SOC}} \cong -\zeta + \frac{1}{2}\frac{\zeta^2}{|E_X - E_A|} \tag{13}$$

will reach the value $-\zeta = 520\ \mathrm{cm}^{-1}$. This is in line with the familiar formula for the fine-structure splitting in diatomic molecules with (Λ, S) coupling,[34]

$$E(\Lambda S \Sigma) = E(\Lambda S) + A \Lambda \Sigma \tag{14}$$

(for $A\ ^2\Pi$: $\Lambda = 1$, $S = \frac{1}{2}$, $\Sigma = \pm\frac{1}{2}$). The molecular fine-structure constant A is given by ζ which was assumed to be R independent in our semiempirical treatment. Since SOC affects the X and A_2 states mainly at rather large separations ($R > 4.0a_0$) we believe that this assumption is reliable. It has also been confirmed by the theoretical calculations of $\zeta(R)$ for HeNe^+ by Cooper.[35]

V. POTENTIAL CURVES

A. $X\ ^2\Sigma_{1/2}^+$ ground state

Table IV contains our potential-energy curves of the $X\ ^2\Sigma_{1/2}^+$ state calculated in different approximations using the X-72 basis set. Most of the curves in Table IV are corrected for spin-orbit coupling and recalculated relative to the common asymptotic value $V(\infty) = 0$; hence these interaction energies have values different from those presented in Table III. In order to visualize the effect of SOC along the full range of distances, the original CEPA(SD) curve is also presented. The SCF potential curve has been included in Table IV in order to show its inductive character and its similarity to the potential curves of the A states, as discussed later and presented in Table V.

The SCF potential curve bears no resemblance to either the experimental RKR curve[3,4] or the curves after inclusion of electron-correlation effects. It exhibits a rather shallow minimum between 3.5 and $4.0a_0$ with a well depth of only 2.7 mhartree = 0.073 eV, which is less than one tenth of the well depth reported by Dabrowski and Herzberg.[3] At SCF level the X state is described by the electronic configuration (1); at large separations the 3σ orbital is essentially the $1s$(He) orbital and 4σ the $2p\sigma$(Ne) orbital. At smaller separations these two σ orbitals are mixed, but the chemical bond formed by the doubly occupied bonding 3σ orbital is nearly outweighted by the singly occupied antibonding 4σ orbital.

As soon as electron correlation is taken into account the position of the minimum as well as the well depth change dramatically; for all basis sets used here and for all methods we have applied, the equilibrium distance is close to $2.75a_0 = 1.46$ Å, in agreement with previous calculations of other authors.[14–16,23] The well depth, however, depends crucially on the computational method; both inclusion of singles and estimate of the effect of unlinked clusters of doubles are compulsory, as we have already discussed in Sec. III. The quality of the basis set,

TABLE IV. Potential-energy curves of the $X\ ^2\Sigma_{1/2}^+$ ground state of HeNe^+ (spin-orbit coupling included, X-72 basis). All interaction energies are in mhartrees.

	SCF	CEPA(SD)			MRCI(SD)	
R/a_0	without SOC[a]	without SOC	with SOC	with SOC	with SOC, DC[b]	with SOC, EDC[c]
2.0	+90.847	+50.566	+52.487	+48.999	+46.035	+44.696
2.2	+47.525	+7.628	+9.447	+6.179	+3.193	+1.926
2.4	+24.392	−12.938	−11.253	−13.885	−16.752	−17.831
2.6	+11.672	−20.798	−19.223	−21.160	−23.742	−24.562
2.8	+4.520	−22.022	−20.523	−21.688	−23.872	−24.427
3.0	+0.563	−20.101	−18.740	−19.082	−20.826	−21.165
3.2	−1.500			−15.412	−16.728	−16.922
3.5	−2.665	−11.645	−10.496	−10.284	−11.052	−11.142
4.0	−2.531	−5.795	−4.921	−4.700	−4.939	−4.981
4.38	−2.004	−3.462	−2.884	−2.708	−2.791	−2.812
4.6	−1.705	−2.612	−2.199	−2.062	−2.105	−2.117
5.0	−1.249	−1.669	−1.456	−1.346	−1.359	−1.363
6.0	−0.584	−0.671	−0.633	−0.580	−0.579	−0.579
7.0	−0.303	−0.336	−0.322	−0.295	−0.294	−0.294
8.0			−0.182	−0.167	−0.167	−0.167
9.0			−0.113	−0.103	−0.103	−0.103
10.0			−0.075	−0.067	−0.067	−0.067

[a] Spin-orbit coupling.

[b] Davidson correction, Eqs. (3)–(5).

[c] Empirical Davidson correction, Eq. (5), constant scaling factor $f = 1.10$. This is our recommended potential curve for the $X\ ^2\Sigma_{1/2}^+$ state; it is the basis of the results presented in Table VII.

on the other hand, seems to be of minor importance; the basis sets X-34, X-50, and X-72 gave comparable results for the well depth; cf. Table III.

One should note that the MRCI(SD) potential curve uncorrected for unlinked-cluster effects does not differ much from the CEPA(SD) potential in the region of small and intermediate distances ($R < 4.0a_0$). Inclusion of these effects by the Davidson correction technique (3)–(5) changes first of all the well depth, and in consequence also the slope of the potential. Furthermore, the use of different scaling factors f in the Davidson correction influences mainly the region of the minimum without essential change of the slope of the potential.

The origin of the large correlation contribution to the interaction energy is obvious: the He atom, i.e., the 3σ orbital occupied by two electrons, is partly pulled into the valence shell of Ne^+. At intermediate and small internuclear separations we therefore have a system containing nine valence electrons, while asymptotically we have two systems with seven and two electrons, respectively. The total correlation energy increases with decreasing R because of the increase of the electron density. This density effect, sometimes referred to as "molecular correlation energy," is responsible for a rather large reduction of barrier heights in certain chemical reactions.[40]

B. $A\,^2\Pi$ states

The two $A\,^2\Pi$ states of $HeNe^+$ with the electronic configuration

$$1\sigma^2 2\sigma^2 3\sigma^2 1\pi^3 4\sigma^2 \tag{15}$$

show no genuine chemical bond, but only a van der Waals minimum. The inductive interaction is in this case the main contribution, since one of the subsystems carries a positive charge; the long-range behavior of the potential is therefore given by

$$V_{\mathrm{ind}} = -\tfrac{1}{2}\alpha_{\mathrm{He}} R^{-4} \; . \tag{16}$$

The experimental value for the static dipole polarizability α_{He} of He is 1.384 a.u.; the SCF value is 1.322 a.u.[41]

Table V contains our results for the $A\,^2\Pi$ potential curves as calculated with basis sets A-56 (SCF only) and A-67 [SCF and CEPA(SD)]. For comparison with the SCF potential curves we have also included the purely inductive interaction (16) calculated with the SCF value of α_{He}. The CEPA(SD) result has been accepted as our final potential curve of the $A_1\,^2\Pi_{3/2}$ state. Our final potential curve of the $A_2\,^2\Pi_{1/2}$ state presented in Table V is the result of the spin-orbit interaction between the CEPA(SD) potential of the A state and the MRCI(SD)-EDC potential of the X state (cf. Table IV). We have chosen this variant for the X state because it yields the best results for spectroscopic properties of this state, as discussed in Sec. VI.

The following observations can be made.

(1) The total well depth without SOC is only in the order of 1.1 mhartree = 240 cm^{-1}, therefore basis-set superposition errors are important. These effects have been estimated by the counterpoise method of Boys and Bernardi.[42] Table V shows that the counterpoise correction (CC) is particularly important at SCF level; for our basis A-67 with many diffuse p atomic orbitals (AO's) on He (in order to allow for the polarization of He by Ne^+) CC amounts to 250 μhartree, i.e., to about 25% of the interaction energy itself near the minimum of the potential curve. The CC to the correlation energy is much smaller, only 10–15 % of the CC to the SCF energy. Due to the basis-set superposition error the uncorrected minimum for the smaller A-56 basis is even deeper than that for A-67, but with CC the results for the two basis sets agree

TABLE V. Potential-energy curves for the $A\,^2\Pi$ states of $HeNe^+$. All interaction energies are in mhartrees.

Basis[a]	A-56	A-67				A-67	
method	SCF	SCF				CEPA(SD)	
R/a_0	without CC	without CC	CC[b]	V^c_{ind}	without CC	CC[b,e]	CC[b],SOC[d,f]
3.5		+5.920	+6.575		+4.933	+5.776	+4.737
4.0	−0.094	+0.129	+0.574	−2.582	−0.437	+0.112	−0.697
4.38	−1.137	−0.934	−0.615	−1.796	−1.341	−0.957	−1.477
4.6	−1.278	−1.084	−0.821	−1.476	−1.404	−1.103	−1.458
5.0	−1.206	−1.039	−0.845	−1.058	−1.253	−1.020	−1.170
5.5	−0.968	−0.831	−0.682	−0.722	−0.963	−0.799	−0.820
6.0	−0.739	−0.635	−0.510	−0.510	−0.722	−0.586	−0.583
7.0	−0.421	−0.372	−0.282	−0.275	−0.412	−0.317	−0.305
8.0	−0.240	−0.227	−0.165	−0.161	−0.246	−0.182	−0.175
9.0	−0.136	−0.145	−0.103	−0.101	−0.156	−0.113	−0.108
10.0	−0.080	−0.098	−0.066	−0.066	−0.106	−0.075	−0.071

[a] Compare Table I.

[b] Counterpoise correction, Ref. 42, included.

[c] Inductive potential, Eq. (16).

[d] Spin-orbit coupling included; Eq. (9) and the MRCI(SD)-EDC and CEPA(SD)-CC energies for E_X and E_A, respectively, have been used.

[e] This is our recommended potential curve for the $A_1\,^2\Pi_{3/2}$ state; it is the basis of the results presented in Table VIII.

[f] This is our recommended potential curve for the $A_2\,^2\Pi_{1/2}$ state; it is the basis of the results presented in Table VIII.

within about 20 μhartree (this is not documented in Table V, but has been checked for several values of R). We should mention that the CC to the X-state potential has also been calculated, but due to the larger sp part of the X-72 basis it is almost negligible (about 60 μhartree for $R = 2.8a_0$) and has not been included in Table IV.

(2) Since the inductive interaction is taken care of by the SCF approximation, we expect that the $A\ ^2\Pi$ potential is fairly well described already at this level. The comparison of V_{ind}, SCF, and CEPA results in Table V shows that this is indeed the case, at least for $R > 6.0a_0$; even in the vicinity of the minimum, one obtains about 75% of the interaction energy at SCF level. Electron correlation further deepens the minimum by about 250 μhartree and shifts it to smaller R, since it describes the dispersion interaction which is asymptotically proportional to R^{-6}.

(3) SOC has an important effect on the shape of the A_2-state potential curve; the well depth increases to 1.5 mhartree = 328 cm^{-1} and is shifted to a smaller R value, in reasonable agreement with experiment. These changes have an essential influence on the calculated spectroscopic properties of this state.

VI. MOLECULAR CONSTANTS

Using the potential curves presented in Tables IV and V we have calculated some molecular properties for HeNe^+ in its lowest electronic states (X, A_1, and A_2) and compared them with the corresponding values resulting from experiment[3] or from semiempirical model calculations.[5] These results are collected in Tables VI–VIII. In order to show how important SOC effects are, we have also included in Table VI for the X state some results obtained without SOC; for the A states these effects are visible in Table VIII just by comparing the properties of the A_1 and A_2 states, because only the A_2 state is influenced by SOC.

Each of the potential curves has been least-squares fitted to a high-order polynomial in R^{-1}. These interpolated potentials were used for a precise determination of R_e and D_e as well as for a calculation of vibrational energies $G(v)$ and rotational constants B_v by numerical integration of the vibrational Schrödinger equation. Molecular constants such as ω_e, $\omega_e x_e$, etc. were calculated by a least-squares fit of all bound vibrational levels to a Dunham-type formula. A set of these results for $^4\text{HeNe}^+$ is shown in Table VI for the X state (calculated using different potential curves) and in Table VIII (upper part) for the two A states. Analogous calculations for $^3\text{HeNe}^+$ have also been performed but are not documented here. Instead of presenting derived quantities such as $\omega_e x_e$, $\omega_e y_e$, B_e, α_e, etc., we compare in Table VII (for the X state) and Table VIII (for the A states) the calculated and experimental values of directly measurable quantities for both isotopic species: vibrational intervals $\Delta G(v+\frac{1}{2})$ and rotational constants B_v.

As we have already mentioned in Sec. IV, SOC has almost no effect on the potential curve of the $X\ ^2\Sigma^+_{1/2}$ ground state in the vicinity of its equilibrium distance. The results in Table VI show that none of the properties that sample mainly this region (R_e itself, D_e, ω_e) is changed by SOC, except for D_e, which is reduced by about 300 cm^{-1} due to the spin-orbit energy contribution to the asymptotic $^2P_{3/2}$ ground state of Ne^+. Our CEPA results for these properties still differ considerably from the corresponding experimental values,[3] whether SOC is included or not. In particular, our R_e value is larger by 0.16 Å than that of Dabrowski and Herzberg,[3] but in reasonable agreement with the results of all previous *ab initio* calculations (without SOC): $R_e = 1.49$ Å (CI calculations of Blint[15]); 1.473 and 1.485 Å (valence-bond calcu-

TABLE VI. Molecular constants calculated in different approximations for the $X\ ^2\Sigma^+_{1/2}$ ground state of $^4\text{HeNe}^+$ (basis X-72, spin-orbit coupling included). R_e, σ in Å, other values in cm^{-1}.

Method	CEPA(SD)		MRCI(SD)				Semiemp.
Property	without SOC[a]	with SOC	with SOC	DC[b]	EDC[c]	Expt.[d]	model[e]
D_e	4854	4542	4831	5342	5492	6216±300[f]	6154±246
R_e	1.457	1.463	1.438	1.431	1.425	1.300[f]	1.38±0.05
σ[g]	1.194	1.202	1.188	1.176	1.171		1.138
ω_e[h]	821	819	856	899	913	1308	
$\Delta G(6\frac{1}{2})$[i]	304	250	265	333	349	341.59	
$\Delta G(7\frac{1}{2})$	208	153	161	215	229	233.42	
$\Delta G(8\frac{1}{2})$	130	90	90	125	135	146.27	

[a] Spin-orbit coupling.

[b] Davidson correction, Eqs. (3)–(5).

[c] Empirical Davidson correction, Eq. (5) with a constant scaling factor $f = 1.10$; these are our recommended values.

[d] Reference 3.

[e] Reference 5.

[f] Values for $^4\text{HeNe}^+$; the corresponding values for $^3\text{HeNe}^+$ are $D_e = 6237\ \text{cm}^{-1}$, $R_e = 1.330$ Å.

[g] Hard-core radius, defined by $V(\sigma) = V(\infty)$.

[h] ω_e's were calculated by a least-squares fit of the Dunham-type formula to all bound vibrational levels; they are not directly comparable with the experimental values.

[i] $\Delta G(v+\frac{1}{2}) \equiv G(v+1) - G(v)$.

TABLE VII. Vibrational intervals ΔG and rotational constants B_v for the $X\,^2\Sigma^+_{1/2}$ ground state of HeNe$^+$. All entries are in cm^{-1}.

	^{4}HeNe$^+$ [a]				^{3}HeNe$^+$ [a]			
	Experiment[b]		This work		Experiment[b]		This work	
v	ΔG[c]	B_v	ΔG	B_v	ΔG	B_v	ΔG	B_v
0			902	2.450			1009	3.109
1			834	2.351			916	2.965
2			749	2.232			807	2.790
3			660	2.105			692	2.599
4			568	1.963			570	2.386
5			467	1.805	414.58	2.101 3	427	2.129
6	341.59	1.589 83	349	1.610	275.78	1.779 51	272	1.790
7	233.42	1.357 55	229	1.361	163.42	1.398 59	150	1.392
8	146.27	1.090 37	135	1.083		1.040 0	75	1.007
9		0.843 1	73	0.814				0.675
10				0.577				

[a] Isotope masses from Ref. 43.

[b] Reference 3.

[c] $\Delta G(v+\frac{1}{2})\equiv G(v+1)-G(v)$ is given in the lines labeled v.

lations of Kendrick and Kuntz[16] with two different basis sets); 1.46 Å (CASSCF calculation by Hotokka[23]). Likewise, our results for D_e, ω_e, etc. are completely different from experiment, but very similar to those which can be calculated from the potential curves reported in Ref. 16. Inclusion of triple excitations with the MRCI(SD) approach, with further corrections for unlinked-cluster contributions by the Davidson correction technique results in only slight changes of the calculated spectroscopic constants towards the experimental values. Our recommended values from the MRCI(SD)-EDC curve are still different from experiment[3] by 0.12 Å for R_e (but in reasonable agreement with the semiempirical estimate of Ref. 5) and by 700 cm^{-1} for D_e.

For the $A\,^2\Pi$ states the situation looks much better. Our procedure of semiempirically including SOC effects

TABLE VIII. Molecular constants, vibrational intervals ΔG, and rotational constants B_v for the two $A\,^2\Pi$ states of HeNe$^+$. R_e, σ in Å, other values in cm^{-1}.

State / Property	$A_2\,^2\Pi_{1/2}$ Experiment[a]	$A_2\,^2\Pi_{1/2}$ Semiemp. model[b]	$A_2\,^2\Pi_{1/2}$ This work	$A_1\,^2\Pi_{3/2}$ Semiemp. model[b]	$A_1\,^2\Pi_{3/2}$ This work
D_e	347.2[c]	380±20	328	282±20	243
R_e	2.318 60[c]	2.38±0.05	2.362	2.38±0.05	2.463
σ[d]		2.01	2.054	2.06	2.128
ω_e[e]	129.69		190		132

v	ΔG[f]	B_v	ΔG	B_v	ΔG	B_v
			^{4}HeNe$^+$ [g]			
0	129.69	0.865 71	119	0.840	87	0.752
1		0.716 58	68	0.674	53	0.602
2			37	0.508	27	0.439
3				0.369		0.295
			^{3}HeNe$^+$ [g]			
0	138.5	1.090 0	126	1.056	93	0.944
1		0.885	66	0.816	51	0.728
2				0.579		0.498

[a] Reference 3.

[b] Reference 5.

[c] Values for ^{4}HeNe$^+$; the corresponding values for ^{3}HeNe$^+$ are $D_e=341.0$ cm^{-1}, $R_e=2.3226$ Å.

[d] Hard-core radius, defined by $V(\sigma)=V(\infty)$.

[e] For ^{4}HeNe$^+$; ω_e's were calculated by a least-squares fit of the Dunham-type formula to all bound vibrational levels; they are not directly comparable with the experimental values.

[f] $\Delta G(v+\frac{1}{2})\equiv G(v+1)-G(v)$.

[g] Isotope masses from Ref. 43.

largely reduces the discrepancy between experiment and the SOC-uncorrected results for the A_2 state, while the A_1 state is not influenced by SOC. For the A_2 state the equilibrium distance R_e is shifted by SOC by as much as 0.10 Å to smaller values and the well depth is increased by 35%. The calculated properties of the A_2 state are in fair agreement with experiment;[3] an error of 0.04 Å for R_e for a very shallow potential can be considered as tolerable. Our results for both A states fit also well with the semiempirical predictions of Hausamann and Morgner.[5] The main discrepancy between our predictions and the analysis of Ref. 3 (but not Ref. 5!) concerns the number of bound vibrational levels; since SOC has deepened the potential well without changing the long-range behavior ($R > 5.0a_0$) too much, the A_2 state has even more bound vibrational levels (4) than the A_1 state (3). This contradicts the experimental observation[3] of only one vibrational interval $\Delta G(\frac{1}{2})$ for A_2. It seems unlikely that a more accurate treatment of SOC will change the A_2 potential in the region $4.5 < R < 5.0a_0$ as much as to reduce the number of bound levels to 2. Carrington and Softley[4] could not assign 29 of the observed lines to the vibration-rotation spacings reported in Ref. 3. On the basis of their excess energy measurements they suggested the existence of at least two more vibrational levels ($v = 2,3$) in this state. Our results are in full agreement with this suggestion.

Tables VII and VIII contain vibrational intervals $\Delta G(v+\frac{1}{2})$ and rotational constants B_v, as calculated from our recommended potential curves for the states X, A_1, A_2. This enables us to make a direct comparison of observed and calculated quantities and seems to be particularly necessary for HeNe$^+$, since an evaluation of ω_e, $\omega_e x_e$, etc. is not possible for the A_2 state (only one ΔG observed) and since the shape of the potential curve of the X ground state does not allow us to extrapolate from $v = 6,7,8$ down to $v = 0$.

Indeed, a calculation of Dunham-type spectroscopic parameters such as ω's for the X state from higher vibrational levels only is connected with very large uncertainties; we have calculated these parameters from our $\Delta G(v+\frac{1}{2})$, $v = 6,7,8$ from Table VII and have obtained values which are very similar to those reported in Ref. 3, but completely different from the values calculated on the basis of the least-squares fit to all bound vibrational levels. This means that one cannot describe the vibrational spectrum, i.e., the whole potential curve, with just three Dunham parameters ($\omega_e, \omega_e x_e, \omega_e y_e$).

For the A_2 state the only observed vibrational interval $\Delta G(\frac{1}{2})$ is rather close to our result, and the same is true for B_0 and B_1; the still existing deviations from the experimental results are in the same order of magnitude (0.04 cm^{-1} for B_v, 10 cm^{-1} for ΔG) as for the ground state.

VII. CONCLUSIONS

The specific difficulties that we have encountered in our calculations for the three lowest electronic states of HeNe$^+$ were the following.

(1) The moderately strong chemical bond in the $X\,^2\Sigma^+_{1/2}$ ground state is essentially due to electron-correlation effects. In calculating them we found remarkably large differences between CI and CEPA results as well as between calculations with and without the inclusion of singly excited configurations. Moreover, in order to describe these correlation effects correctly it is necessary to include a special class of triply excited configurations—those which are doubly excited relative to the leading configuration of the higher $B\,^2\Sigma^+_{1/2}$ state. We have applied the MRCI(SD) approach, which alone, however, suffers from the size-inconsistency error, and had to be further improved using the Davidson correction technique.

(2) The $A\,^2\Pi$ states with their very shallow inductive minima require large basis sets including, in particular, diffuse p-type AO's on He. The counterpoise correction for basis-set unsaturation effects is compulsory as well. For this state, correlation effects are of minor importance.

(3) Spin-orbit coupling between $X\,^2\Sigma^+_{1/2}$ and $A_2\,^2\Pi_{1/2}$ dramatically changes the shapes of both potential curves at intermediate distances ($3.5 < R < 6.0a_0$). This has large effects on all spectroscopic properties of the A_2 state and on the higher vibrational levels of the X state. Our simple semiempirical treatment of SOC with an R-independent spin-orbit coupling constant ζ describes these effects correctly.

Despite of the uncertainties caused by these difficulties we think that our results are reliable enough to justify the following comments on the analysis of the experimental spectrum of HeNe$^+$.[3]

(4) The shape of the potential curve of the $X\,^2\Sigma^+_{1/2}$ ground state does not allow the calculation of ω_e, $\omega_e x_e$, and $\omega_e y_e$ from the observed intervals between higher vibrational levels. The values reported in Ref. 3 for these constants are incorrect, and the bond distance extrapolated from these high levels is too small (with a large difference for two isotopic molecules); the dissociation energy resulting from such extrapolations is too large.

(5) For the $A_2\,^2\Pi_{1/2}$ state our calculations are in agreement with the analysis of Ref. 3; we only expect the existence of more than two vibrational levels because of the R^{-4} long-range behavior of the potential curve; our predictions are in agreement with the suggestion of recent experimental measurements[4] and a semiempirical analysis.[5]

(6) The two components (A_1 and A_2) of the $A\,^2\Pi$ state are quite different, because spin-orbit coupling causes a first-order interaction between the A_2 and X states, but does not affect the A_1 state.

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