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Ab initio calculations of energy transfer and non-additivity in the He-Ne laser system

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Abstract. *Ab initio* calculations were performed for several suggested mechanisms of energy transfer between helium metastable particles and neon. Optimized geometries and excited-state energies were calculated for neon excited-state complexes and the convergence properties of the non-additive contributions to the interaction energies were examined. The most probable excitation-transfer mechanism was found to be $\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{He_2Ne})_r^* \to \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He}$ based on an energy difference of 0.0674 eV between the triplet excited state of He_2^m and the singlet excited state of $(\mathrm{HeNeHe})_r^*$. No theoretical evidence was found for the production of neon singlet excited-state complexes other than 20.0858 to 20.4875 eV by the considered two-, three- and four-body models of energy transfer processes. The energy curves of the reactions involving the excited-state complexes $(\mathrm{HeNeHe})_r^*$ and $(\mathrm{HeNe})_r^*$ are provided and compared with the previously reported experimental results on the reaction $\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{He_2Ne})_r^* \to \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He}$. The relation between the probability of energy transfer and laser activity is discussed. The non-additive contribution to the total interaction energy of the nominated $(\mathrm{HeNeHe})_r^*$ intermediate complex was found to be negligible, pointing to the possibility of constructing model potentials and simulation of larger systems.

PACS. 34.20.-b Interatomic and intermolecular potentials and forces, potential energy surfaces for collisions – 31.30.-i Corrections to electronic structure – 31.50.+w Excited states

1 Introduction

The importance of energy transfer mechanisms between helium molecular metastable species and neon atoms has been investigated by experimental afterglow studies on helium-neon plasmas in both stationary and flowing gas systems, over a wide range of pressures and mixture ratios [1–5]. The interaction of metastable $\mathrm{He}(2\ ^3S)$ and $\mathrm{He}(2\ ^1S)$ atoms with Ne was experimentally studied employing cross atomic beams technique [6–10]. The interaction $\mathrm{He}^* + \mathrm{Ne}$ potentials in $^3\Sigma^+$ $(\mathrm{He}(2\ ^3S) + \mathrm{Ne})$ and $^1\Sigma^+$ $(\mathrm{He}(2\ ^1S) + \mathrm{Ne})$ states were calculated employing various versions of single-electron method of model potential or pseudopotential [11]. For the analysis of excitation transfer process, the repulsive part of interaction potentials $U\ (^1\Sigma, R)$ and $U\ (^3\Sigma, R)$ of $\mathrm{He}(2\ ^3S, 2\ ^1S) + \mathrm{Ne}$ interactions, where $U(R) \geq 10$ meV are of particular interest. The potentials $U\ (^1\Sigma, R)$ [6] and $U\ (^3\Sigma, \mathrm{R})$ [7] are the most reliable in the repulsive region. These potentials were reconstructed from data of differential scattering in the wide range of relative scattering energies $-25\ \mathrm{meV} \leq E \leq 370\ \mathrm{meV}$.

In 1980, Ernie and Oskam [12] used light absorption and emission spectroscopy to study the time dependence of the $\mathrm{He}^m(2\,^3S)$, $\mathrm{He}_2^m(a^3\Sigma_u^+)$, and $\mathrm{Ne}^m(^3p_2)$ number densities and spectral emission intensities from 19 $\mathrm{Ne_I}$ states during the afterglow of helium-neon discharges. The $\mathrm{Ne_I}$ states below 20.56 eV were produced and $\mathrm{Ne}(2p^5 3s)$ states were found by the dissociative excitation-transfer mechanism $\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{He_2Ne})_r^* \to \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He}$ involving intermediate repulsive state. In 1989, Devardini, Zagrebin and Blagoev performed an analysis for the available experimental and theoretical results about excited heteronuclear quasimolecular states of noble gases in a review article [13]. In 1989, Fukuyama and Siska [14] combined $\mathrm{He}^*(2\ ^3S) + \mathrm{Ne}$ differential elastic scattering measurements in crossed supersonic beams with total crossed supersonic beams with total cross-section velocity dependence and quenching rate constant temperature dependence to determine a 3 × 3 potential matrix characterizing a double curve-crossing model for the collision dynamics and energy transfer. In 1990, Martin, Fukuyama and Siska [15] reported a multichannel analysis of $\mathrm{He}^*(2\ ^1S) + \mathrm{Ne}$ elastic and inelastic scattering in crossed atomic beams. Their model suggests the importance of intermediate “chaperone” states, in which the excited electron is temporarily trapped in a d or f Rydberg Ne orbital, in channeling flux into the $4s'$ and $5s'$ upper laser states of Ne by energy transfer from $\mathrm{He}^*(2\,S\ ^{1/3}S)$. In 1992, Devardini, Zagrebin and Blagoev reviewed the transfer in He-Ne collisions at thermal energies [16]. The energy transfer in He $(2\ ^{1,3}S,\ 2\ ^{1,3}P)$ collisions and

Ne*-He collisions were the main content of the review. In 1993, McLaughlin, Gillan, Burke and Dahler [17] performed *ab initio* calculations on the e^--He_2^+ complex using the R-matrix technique. Elastic cross-sections were presented for selected bond lengths in the range 1.5–4.0 a_0 for the $^3\Sigma_u^+$ total symmetry. In relation to energy transfer, if the helium molecular metastable state is nearly resonant with the corresponding neon metastable state, the collision process should result in excitation energy transfer and hence pumping of the HeNe laser system. The pumping of neon in the helium-neon gas laser depends on a coincidental matching of the helium and neon energy separations, so that excited helium can transfer excess energy to neon during a collision and the probability of a collision depends on the degree of coincidental matching.

Despite the fact that there has been a considerable interest in the role of non-additivity of closed-shell atoms and ions in their ground states [18], very little is known either experimentally or theoretically about the size or functional form of non-additivity in the excited-state complexes of He-Ne. From the calculations which have been performed on small clusters of atoms with all the interparticle distance equal or not too dissimilar, it appears that individual m-body terms are usually smaller than $m-1$ body terms, but do not necessarily converge rapidly. Inert gas clusters in their ground electronic states received the most attention [19]. At both short-range X and around the van der Waals minimum Y the interaction energy was dominated by pair terms. However, at very close separations this was no longer true [20]. The role of non-additivity for systems with $(n \geq 3)$, where (n) is the number of interacting particles, is therefore a prerequisite for constructing model potentials and simulation of larger systems. Since the HeNe laser is basically an excited-state system, the role of non-additivity in He-Ne excited-state complexes should be of interest.

As shown, published *ab initio* calculations concerning the reaction mechanism for energy transfer between the helium molecular metastable state and neon, energy curves of reactions involving excited-state complexes as well as the role of non-additivity in these complexes are still scarce. In the present study, an attempt has been made to address these topics using the CIS methods of *ab initio* theory.

2 Methods and calculations

2.1 Interaction energies

Interaction energies were calculated by subtracting the asymptotic energies (rather than the monomer energies) from the total energies to minimize the size extensivity error of the truncated CIS expansion. Approximations which have the property that the calculated energy varies linearly with the number of particles as the size of the subsystem increases are said to be size extensive. It follows that size extensivity means that calculations under the assumption of infinite distance between the monomers should yield the sum of the monomer energies. For truncated CI methods, the energy of two non-interacting subsystems is not twice the energy of one of them, calculated in the same approximation. Several evidences for the importance of the size extensivity error (SEE) in the truncated CI methods were obtained. Since SEE can be as large as the stabilization energy itself, it must be eliminated. Elimination can be done either rigorously by including all types of excitations in the CI method or partially by subtracting the energy of the supersystem at infinite distance from the energy of the same supersystem at its equilibrium. Since the size extensivity error of the truncated CIS method employed in the present calculations has been minimized, the major source of errors left will be the neglect of higher-order terms of the CIS expansion. The CIS method named CI-Singles uses the configuration interaction approach and model excited states as combinations of single substitutions out of the Hartree-Fock ground state. CI-Singles is comparable to Hartree-Fock theory for ground-state systems in that it is qualitatively accurate if not always highly quantitatively predictive. Despite this comparison, the CI-Singles method does include some electron correlation [21]. A second source of error in the present calculations is the basis set superposition error (BSSE). This error has been minimized in the present calculations by using the basis set $6-311++G(3df,3pd)$ and is relatively less important than the SEE at the Hartree-Fock and electron correlation levels as proved in a comparative study for errors in HeH^- weak van der Waals interaction potentials [22]. The neglect of zero-point vibrational energies may also affect the accuracy of the calculated energies.

2.2 Non-additivity

The calculations of pairwise (additive) and non-pairwise (non-additive) contributions to the total interaction energy of a microcluster may be carried out using the following scheme.

If the total energy $E(n)$ of a microcluster of (n) interacting atoms is written as

$$E = \sum_{m\geq 1}^{n} E(m,n) = \sum_{i}^{n} E(1,n)_i + \sum_{i<j}^{n} E(2,n)_{ij} + \sum_{i<j<k}^{n} E(3,n)_{ijk} + \ldots + E(n,n)_{ijk\ldots n}\,.$$

The total interaction energy $\Delta E(n)$ will be obtained by subtracting the monomer energies from the total energy:

$$\Delta E(n) = \sum_{m\geq 1}^{n} E(m,n) - \sum_{i}^{n} E(1,n)_i = \sum_{i<j}^{n} E(2,n)_{ij} + \sum_{i<j<k}^{n} E(3,n)_{ijk} + \ldots + E(n,n)_{ijk\ldots n}\,.$$

The first, second, through (n) terms in the last expression represent the two-, three, through (n)-body contributions to the total interaction energy. There are $n(n-1)/2!$

two-body terms, $n(n-1)(n-2)/3!$ three-body terms and $n(n-1)(n-2)\ldots(n-n)/n!$ body term, where (n) is the number of atoms in the finite cluster and the expansion is claimed to be convergent when the non-pairwise contributions are negligible relative to the pairwise contributions. $E(m,n)$ are the m-body contributions to the total energy of n interacting atoms. If $m=1$, then $E(1,n)_i$ will represent the energy of atom i. If $m=2$, then $E(2,n)_{ij}$ will represent the interaction energy between atoms i and j. The interaction energy between atoms i and j is calculated by subtracting the monomer energies from the total energy of the dimer. If $m=3$, then $E(3,n)_{ijk}$ will represent the sum of interaction energies between atoms i and j, i and k as well as j and k in addition to the three-body term. The cycle is then repeated for $m \geq 4$. In Tables 3 and 4 the following notations will be used:

$$\Sigma E^{(2)} = \sum_{i<j}^{n} E(2,4)_{ij}\,,$$

$$\Sigma E^{(3)} = \sum_{i<j<K}^{n} E(3,4)_{ijk}\,,$$

$$E^{(4)} = E(4,4)_{ijkl}\,,$$

and the ratio

$$\Sigma E^{(n>2)} \Big/ \Sigma E^{(2)}$$

will be considered as a measure for non-additivity.

The internally built $6-311++G(3df,3pd)$ basis has been used in the present calculations. This basis set puts $3d$ functions and $1f$ functions on heavy atoms, $3p$ functions and $1d$ functions on hydrogens, as well as diffuse functions on both, and is fairly adequate for the description of excited states. *Ab initio* calculations were carried out using Gaussian 92 [23].

3 Results and discussion

3.1 Mechanisms of energy transfer and curves of excited-state complexes

Four collision mechanisms are suggested for excitation transfer between the helium molecular metastable state and neon ground state:

$$\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \rightarrow (\mathrm{He}_2\mathrm{Ne})_r^* \rightarrow \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He} + \Delta E\,, \qquad (1)$$

$$\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \rightarrow (\mathrm{HeNe}\,)_r^* + \mathrm{He} \quad \searrow \quad \mathrm{He} + \mathrm{Ne}(2p^5 3s) + \Delta E\,, \qquad (2)$$

$$\mathrm{He}_2^m(a^3\Sigma_u^+)\mathrm{Ne}_2 \rightarrow \mathrm{He}_2 + (\mathrm{Ne}_2)_r^* \quad \searrow\ 2\,\mathrm{He} \quad \searrow\ 2\,\mathrm{Ne}(2p^5 3s) + \Delta E\,, \qquad (3)$$

$$\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne}_2 \rightarrow (\mathrm{He}_2\mathrm{Ne}_2)_r^* \rightarrow 2\,\mathrm{He} + 2\,\mathrm{Ne}(2p^5 3s) + \Delta E\,. \qquad (4)$$

Geometry optimization was performed and excited-state energies were calculated for the helium molecular metastable states $\mathrm{He}_2^m(a^1\Sigma_u^+)$ and $\mathrm{He}_2^m(a^3\Sigma_u^+)$ as well as for different configurations of intermediate neon complexes $(\mathrm{He}_2\mathrm{Ne})_r^*$, $(\mathrm{HeNe})_r^*$, $(\mathrm{Ne})_r^*$ and $(\mathrm{He}_2\mathrm{Ne}_2)_r^*$. We have considered two orientations for $(\mathrm{He}_2\mathrm{Ne})_r^*$ and five configurations for $(\mathrm{He}_2\mathrm{Ne}_2)_r^*$. These are shown together with the corresponding CIS energies, lowest singlet and lowest triplet excited-state energies in Table 1. We have also considered the difference in energy between $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and the corresponding neon singlet excited-state complex as an indirect measure for the probability of excitation energy transfer. The smaller the difference, the larger the probability that a collision should result in excitation energy transfer.

Ernie and Oskam [12] have investigated the energy transfer mechanism:

$$\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \rightarrow (\mathrm{He}_2\mathrm{Ne})_r^* \rightarrow \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He} + \Delta E \qquad (1)$$

in which an intermediate interaction state complex $(\mathrm{He}_2\mathrm{Ne})_r^*$ is created. This state then dissociates *via* a repulsive interaction potential energy curve into the appropriate atomic states with total kinetic energy ΔE. They have shown that the energy difference ΔE between the $\mathrm{He}_2^m(a^3\Sigma_u^+)$ state and the neon $2p^5 3s$ levels is at least 1.18 eV and that the resulting large excess energy must appear as kinetic energy for the reaction products.

Geometry optimization was performed and excited energies were calculated for He_2^m and the two possible orientations of $(\mathrm{He}_2\mathrm{Ne})_r^*$, namely $(\mathrm{HeNeHe})_r^*$ and $(\mathrm{HeHeNe})_r^*$. R_{HeHe}, the bond length of He_2^m was calculated to be 3.8797 Å and the excited-state energies of $\mathrm{He}_2^m(a^1\Sigma_u^+)$ and $\mathrm{He}_2^m(a^3\Sigma_u^+)$ were 22.6232 eV and 20.3271 eV, respectively. The two predicted orientations of $(\mathrm{He}_2\mathrm{Ne})_r^*$ were linear with $R_{\mathrm{HeNe}} = 3.245$ Å in $(\mathrm{HeNeHe})_r^*$ and $R_{\mathrm{HeHe}} = 2.632$ Å and $R_{\mathrm{HeNe}} = 3.1851$ Å in $(\mathrm{HeHeNe})_r^*$. The lowest singlet and triplet excited states were calculated to be 20.2597 eV and 19.5613 eV, respectively, for $(\mathrm{HeNeHe})_r^*$ and 20.4647 eV and 19.7149 eV for $(\mathrm{HeHeNe})_r^*$. The energy difference ΔE between $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and the lowest singlet excited states of $(\mathrm{HeNeHe})_r^*$ and $(\mathrm{HeHeNe})_r^*$ were calculated to be 0.0674 eV and 0.1376 eV, respectively. This may lead us to conclude that energy transfer takes place between the triplet excited state of He_2^m and the lowest singlet excited state of the $(\mathrm{HeNeHe})_r^*$ intermediate complex.

Figure 1 shows the energetics of this reaction and contains the energy curves of the $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and $(\mathrm{HeNeHe})_r^*$ states as well as the CIS curves of He_2 and HeNeHe. If it is assumed that the $\mathrm{He}_2^m(a^3\Sigma_u^+)$ species are in the lowest vibrational level ($\nu = 0$), then the energy difference between $\mathrm{He}_2^m(a^3\Sigma_u^+,\ \nu = 0)$ species and the He_2 is, assuming Franck-Condon transitions, $\sim$ 20.3271 eV. However, $\sim$ 20.2597 eV is required for the production of

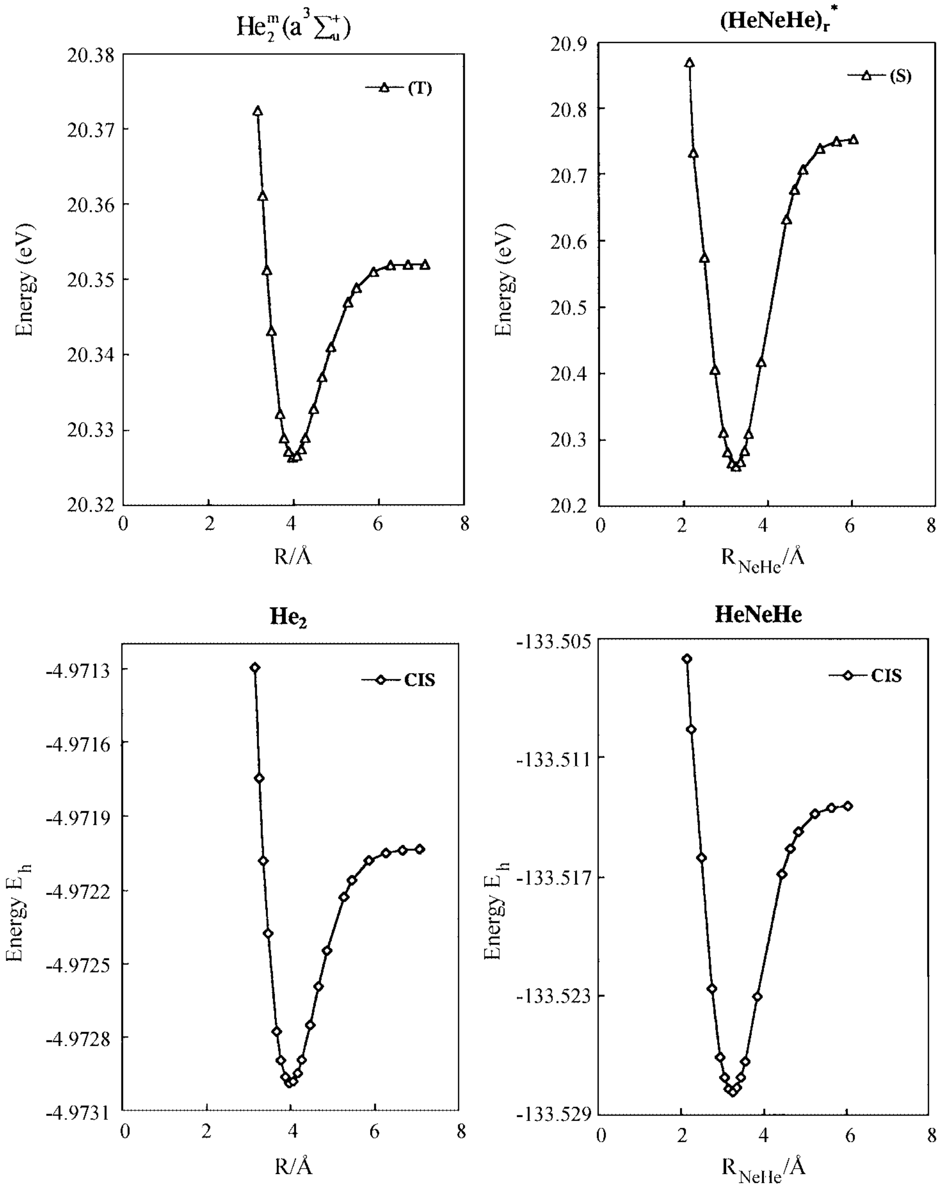

Fig. 1. Energy curves of $\mathrm{He}_2^m(a^3\Sigma_u^+)$ triplet (T) and $(\mathrm{HeNeHe})_r^*$ singlet (S) excited states and the corresponding CIS curves of He_2 and HeNeHe. The energies involved in the transitions are relevant to mechanism (1).

the lowest singlet excited-state complex $(\mathrm{HeNeHe})_r^*$. This implies a discrepancy in the energetics of reaction (1) of 0.0674 eV. Hence, under the stated assumptions, the three-body model for reaction (1) is energetically more favorable than the reaction

$$\begin{array}{l}\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{He}_2)_r + \mathrm{Ne}(2p^53s)\\ \qquad\qquad\qquad\qquad\quad \searrow\\ \qquad\qquad\qquad\qquad\qquad 2\,\mathrm{He} + \Delta E\,,\end{array}$$

to which Ernie and Oskam [12] reported a discrepancy of at least 0.9 eV.

Although the intermediate state $(\mathrm{He}_2\mathrm{Ne})_r^*$ is a three-particle complex and must be treated as such in any exact description, it is possible to gain some insights into the possible reaction mechanisms using two-particle models. One such model would involve the creation of an excited-state helium-neon complex on a repulsive curve. This complex, $(\mathrm{HeNe})_r^*$, would then dissociate with the excess energy ΔE appearing as the kinetic energy of the resulting He and Ne atoms:

$$\begin{array}{l}\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{He\ Ne}\ )_r^* + \mathrm{He}\\ \qquad\qquad\qquad\qquad\qquad \searrow\\ \qquad\qquad\qquad\qquad\qquad\quad \mathrm{He} + \mathrm{Ne}(2p^53s) + \Delta E\,. \quad (2)\end{array}$$

Ernie and Oskam [12] suggested this mechanism and reported that, for such a reaction to occur, a repulsive HeNe excited-state complex with the appropriate energy curve must exist. It is not known whether such a state

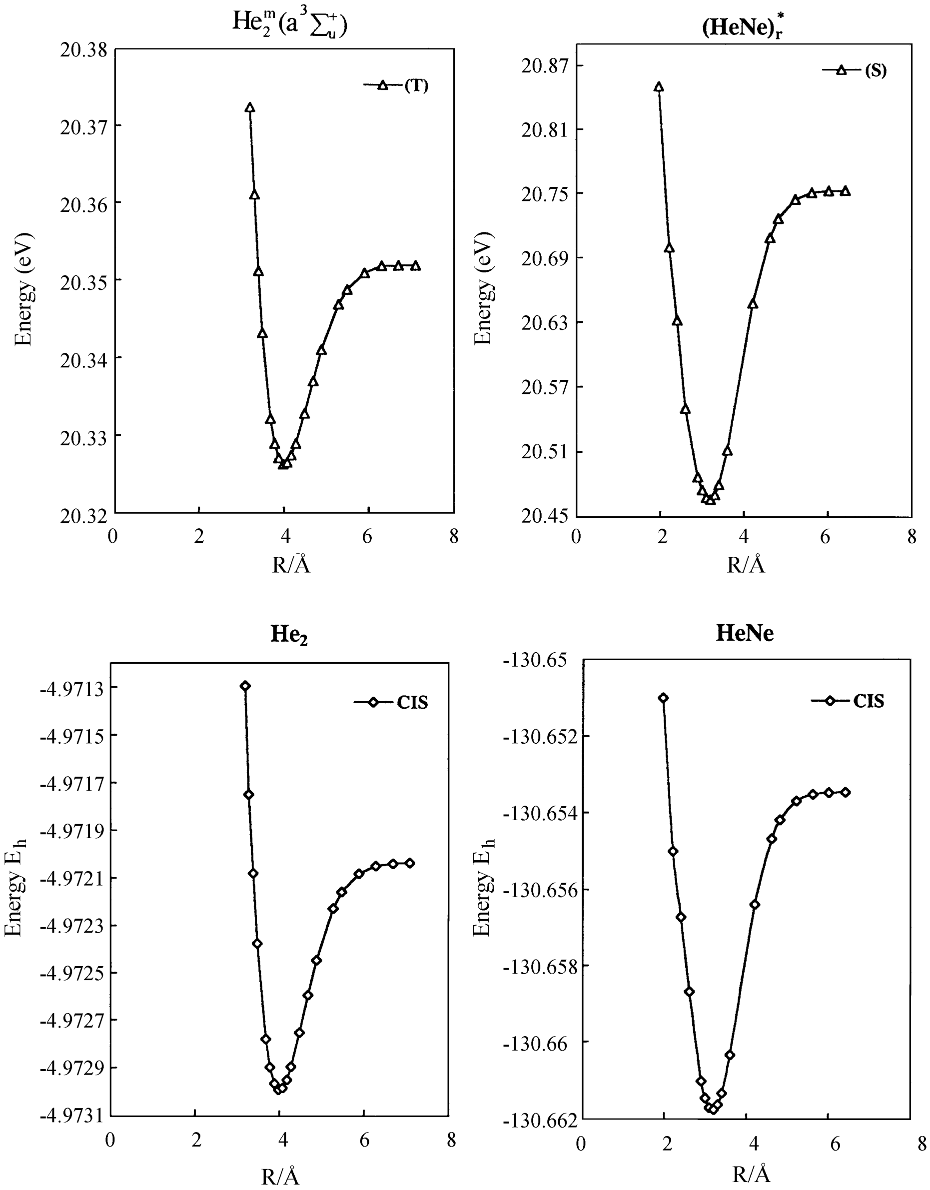

Fig. 2. Energy curves of $He_2^m(a^3\Sigma_u^+)$ triplet (T) and $(HeNe)_r^*$ singlet (S) excited states and the corresponding CIS curves of He$_2$ and HeNe. The energies involved in the transitions are relevant to mechanism (2).

exists nor what the resulting energy curve would be. In an attempt to answer these questions, we have performed *ab initio* calculations for the energetics of this reaction and displayed the energy curves of the $He_2^m(a^3\Sigma_u^+)$ and $(HeNe)_r^*$ states as well as the CIS curves of He$_2$ and HeNe in Figure 2. As stated previously, if it is assumed that the $He_2^m(a^3\Sigma_u^+)$ species are in the lowest vibrational level ($\nu = 0$), the energy difference between $He_2^m(a^3\Sigma_u^+,\ \nu = 0)$ species and He$_2$ is 20.3271 eV, assuming Franck-Condon transitions. However, 20.4663 eV is required for the production of the lowest singlet excited-state complex $(HeNe)_r^*$. This implies a discrepancy in the energetics of reaction (2) of ~ 0.1392 eV. Hence, under the stated assumptions, the two-body model of reaction (2) is energetically more favorable than the reaction

$$\begin{array}{l} He_2^m(a^3\Sigma_u^+) + Ne \rightarrow (He_2)_r + Ne(2p^5 3s) \\ \qquad\qquad\qquad\qquad\qquad\quad \searrow \\ \qquad\qquad\qquad\qquad\qquad\qquad 2\,He + \Delta E \end{array}$$

reported by Ernie and Oskam [12] where a discrepancy of at least 0.9 eV was observed.

Geometry optimization was performed for $(NeNe)_r^*$ and the calculated bond length was 3.2056 Å. The lowest singlet and triplet excited-state energies were 20.4663 eV and 19.7266 eV, respectively. The difference in energy ΔE between $He_2^m(a^3\Sigma_u^+)$ and the lowest singlet excited state of $(HeNe)_r^*$ was 0.1392 eV.

Table 1. Total energies E, lowest excited-state energies of helium molecular metastable state and intermediate neon complexes and the optimal geometries for the considered two-, three- and four-body models of rare-gas clusters at the CIS level using the $6-311++G(3df,3dp)$ basis set.

(1) He_2^m	$E=-4.9729619E_h$	$^1\Sigma_u^+$ 22.6232 eV $^3\Sigma_u^+$ 20.3271 eV	$R=3.87966255$ Å
Two-body models			
(1) $(Ne_2)_r^*$	$E=-256.3267466E_h$	Singlet 20.4875 eV Triplet 19.7741 eV	$R=3.35998012$ Å
(2) $(HeNe)_r^*$	$E=-130.6617401E_h$	Singlet 20.4663 eV Triplet 19.7266 eV	$R=3.20561071$ Å
Three-body models			
(1) $(HeNeHe)_r^*$	$E=-133.5276468E_h$	Singlet 20.2597 eV Triplet 19.5613 eV	$R_{\mathrm{HeNe}}=3.24498912$ Å
(2) $(HeHeNe)_r^*$	$E=-133.5220348E_h$	Singlet 20.4647 eV Triplet 19.7149 eV	$R_{\mathrm{HeHe}}=3.18512836$ Å $R_{\mathrm{HeHe}}=2.63199990$ Å
Four-body models			
(1)$(HeNeHeNe)_r^*$	$E=-262.0547966E_h$	Singlet 20.2498 eV Triplet 19.5537 eV	$R_{\mathrm{HeNe}}=3.2477832$ Å $R_{\mathrm{NeHe}}=3.22564101$ Å $R_{\mathrm{HeNe}}=2.85543954$ Å
(2) $(HeNeNeHe)_r^*$	$E=-262.0535433E_h$	Singlet 20.2528 eV Triplet 19.5915 eV	$R_{\mathrm{HeNe}}=3.2234983$ Å $R_{\mathrm{NeNe}}=3.24149828$ Å
(3) $(NeHeHeNe)_r^*$	$E=-262.0487424E_h$	Singlet 20.4633 eV Triplet 19.7144 eV	$R_{\mathrm{NeHe}}=3.18066807$ Å $R_{\mathrm{HeHe}}=2.60789533$ Å
(4) $\left(\begin{array}{ccc}\mathrm{He} & — & \mathrm{He}\\ \vert & & \vert \\ \mathrm{Ne} & — & \mathrm{He}\end{array}\right)_r^*$	$E=-262.0546483E_h$	Singlet 20.2224 eV Triplet 19.5616 eV	$R_{\mathrm{HeNe}}=3.19659649$ Å
(5) $\left(\begin{array}{ccc}\mathrm{Ne} & — & \mathrm{Ne}\\ \vert & & \vert \\ \mathrm{He} & — & \mathrm{He}\end{array}\right)_r^*$	$E=-262.046721669E_h$	Singlet 20.0858 eV Triplet 19.4408 eV	$R_{\mathrm{HeHe}}=3.44131712$ Å $R_{\mathrm{HeNe}}=4.35328768$ Å $R_{\mathrm{NeNe}}=4.92702283$ Å
	∠HeHeNe = 92.14966702°		∠HeNeNe = 46.94929629°

Other possible reaction mechanisms using the two-particle model may involve the reaction between the molecular metastable state $He_2^m(a^3\Sigma_u^+)$ and the neon ground-state molecule. This model would involve the creation of an excited-state Ne_2 complex on a repulsive curve. This complex $(Ne_2)_r^*$, would then dissociate with the excess energy ΔE appearing as the kinetic energy of the resulting Ne atoms:

$$\begin{array}{l} \mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne}_2 \rightarrow \mathrm{He}_2 + (\mathrm{Ne}_2)_r^* \\ \qquad\qquad\qquad\qquad\quad \searrow \qquad \searrow \\ \qquad\qquad\qquad\qquad\quad 2\,\mathrm{He} \;\; 2\,\mathrm{Ne}(2p^53s) + \Delta E\,. \end{array} \quad (3)$$

Geometry optimization was performed for $(Ne_2)_r^*$ and the calculated bond length was 3.3599 Å. The lowest singlet and triplet excited-state energies were 20.4875 eV and 19.7741 eV, respectively. The difference in energy ΔE between $He_2^m(a^3\Sigma_u^+)$ and the lowest singlet excited state of $(Ne_2)_r^*$ is 0.1604 eV compared with 0.1392 eV for $(HeNe)_r^*$. $(HeNe)_r^*$ is thus a more favorable reactive intermediate than $(Ne_2)_r^*$ as far as the two-body model is concerned.

Finally, we consider the four-body model that involves the creation of an excited He_2Ne_2 complex on the repulsive curve. This complex would then dissociate with the excess energy ΔE appearing as the kinetic energy of the resulting He and Ne atoms, *i.e.*,

$$\begin{array}{l} \mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne}_2 \rightarrow (\mathrm{He}_2\mathrm{Ne}_2)_r^* \rightarrow \\ 2\,\mathrm{He} + 2\,\mathrm{Ne}(2p^53s) + \Delta E\,; \end{array} \quad (4)$$

however, for such a reaction to occur a repulsive He_2Ne_2 excited-state complex with the appropriate energy curve must exist. We have therefore considered five probable orientations for the He_2Ne_2 excited-state complex, see Table 1. Geometry optimization was performed for each orientation. $R_{\mathrm{HeNe}} = 3.2478$ Å, $R_{\mathrm{NeHe}} = 3.2256$ Å and $R_{\mathrm{HeNe}} = 2.8554$ Å for the linear orientation $(HeNeHeNe)_r^*$. $R_{\mathrm{HeNe}} = 3.2235$ Å and $R_{\mathrm{NeNe}} = 3.2415$ Å for the linear orientation $(HeNeNeHe)_r^*$. $R_{\mathrm{NeHe}} = 3.1806$ Å and

Table 2. The energy difference ΔE between $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and singlet excited-state energies of neon complexes. In the last column ΔE are arranged in an ascending order. CIS calculations were carried out using the basis set $6-311++G(3df,3dp)$ at the optimized geometries given in Table 1.

	ΔE/eV	Order of ΔE
Two-body models		
(1) $(\mathrm{Ne}_2)_r^*$	0.1604	(9)
(2) $(\mathrm{HeNe})_r^*$	0.1392	(8)
Three-body models		
(1) $(\mathrm{HeNeHe})_r^*$	0.0674	(1)
(2) $(\mathrm{HeHeNe})_r^*$	0.1376	(7)
Four-body models		
(1) $(\mathrm{HeNeHeNe})_r^*$	0.0773	(3)
(2) $(\mathrm{HeNeNeHe})_r^*$	0.0743	(2)
(3) $(\mathrm{NeHeHeNe})_r^*$	0.1362	(6)
(4) $\begin{pmatrix} \mathrm{He} & — & \mathrm{Ne} \\ \vert & & \vert \\ \mathrm{Ne} & — & \mathrm{He} \end{pmatrix}_r^*$	0.1047	(4)
(5) $\begin{pmatrix} \mathrm{Ne} & — & \mathrm{Ne} \\ \vert & & \vert \\ \mathrm{He} & — & \mathrm{He} \end{pmatrix}_r^*$	0.1190	(5)

$R_{\mathrm{HeHe}} = 2.6079$ Å for the orientation $(\mathrm{NeHeHeNe})_r^*$. $R_{\mathrm{HeNe}} = 3.1966$ Å for the cyclic planar orientation $(\mathrm{HeNeHeNe})_r^*$. $R_{\mathrm{HeHe}} = 3.4413$ Å, $R_{\mathrm{HeNe}} = 4.3533$ Å, $R_{\mathrm{NeNe}} = 4.9270$ Å, $\angle\mathrm{HeNeNe} = 46.9493°$, $\angle\mathrm{HeHeNe} = 92.1497°$ for the cyclic planar orientation $(\mathrm{NeNeHeHe})_r^*$. As shown in Table 2 the smallest energy difference between $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and the singlet excited states of $(\mathrm{He}_2\mathrm{Ne}_2)_r^*$ is assigned to the linear orientation $(\mathrm{HeNeNeHe})_r^*$. It is therefore suggested to be the most favorable reactive intermediate of the four-body model.

The energy difference ΔE between the helium molecular metastable state $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and singlet excited-state complexes of neon are given in Table 2. ΔE are arranged in an ascending order in the last column. As shown from this table the excitation-transfer mechanism

$$\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{HeNeHe})_r^* \to \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He} + \Delta E$$

might be the most probable based on an energy difference of 0.0674 eV. The result is in agreement with the previous prediction of Ernie and Oskam [12] that the $\mathrm{Ne}(2p^5 3s)$ states are formed directly by the dissociative excitation-transfer mechanism

$$\mathrm{He}_2^m(a^3\Sigma_u^+) + \mathrm{Ne} \to (\mathrm{He}_2\mathrm{Ne})_r^* \to \mathrm{Ne}(2p^5 3s) + 2\,\mathrm{He} + \Delta E$$

and may nominate the reactants as candidates for lasing activity involving the $(\mathrm{HeNeHe})_r^*$ intermediate subject to the constraint of the truncated CIS method employed in the present calculations. The second through the ninth priority candidates may then be identified from the last column of Table 2.

Inspection of Table 1 reveals that no theoretical evidence was found for the production of neon singlet excited-state complexes other than 20.0858 eV to 20.4875 eV by the considered two-, three-, and four-body models of energy transfer processes. The result may be compared with the experimental observation of Ernie and Oskam [12] that no evidence was found for the production of $\mathrm{Ne_I}$ energy levels above 20.56 eV by binary energy-transfer processes.

3.2 The role of non-additivity in He-Ne excited-state complexes

Very little appears to be known about the role of non-additivity in small clusters of atoms in their excited electronic states. This situation exists because reasonably accurate pair potentials over a wide range of R are only just becoming available. Most of the previous theoretical work is based on effective pair potentials which are usually derived from solid-state data. Since these effective pair potentials inevitably incorporate some many-body character, they cannot give any information on the size of many-body contributions to bulk or small-cluster properties, in particular the excited-state properties.

It is conventional to divide the total interaction energy of (n) interacting atoms into pairwise additive and non-pairwise additive contributions. The convergence property of the non-pairwise additive contributions is a prerequisite for constructing model potentials and simulation of larger systems. If the non-pairwise additive contributions are negligible relative to the pairwise additive counterparts, the total interaction energy will be well represented as the sum of two-body terms. We are therefore interested in the role of non-additivity. However, this method is based on the assumption that potential energy surfaces only the interaction configuration contributions in a reduced form. The assumption could be rather drastic for an excited state, where the electronic states are expected to be more closely spaced. A logical consequence of this limitation is that the present results must be considered as lower limits to the real interaction.

In Tables 3 and 4, the ground- and singlet excited-state properties of the many-body energies and non-additivities for the considered three- and four-body models are given and CIS calculations were carried out at the optimized geometries given in Table 1. The total interaction energy, as well as the pairwise and non-pairwise additive contributions of the excited-state models were approximately twice those of the ground-state models.

Apart from the (HeNeHeNe) intermediate complex, the non-additivity (last columns of Tab. 2 and 4) of the ground-state models was approximately the same as that of the excited states. With few exceptions, the non-additivity term $E^{(4)}$ was much greater than $\Sigma E^{(3)}$ and opposite in sign. The negative sign of a term implies contribution to the attraction and the positive sign implies

Table 3. Ground-state total interaction energies ΔE, two-, three, and four-body terms ($\Sigma E^{(2)}$, $\Sigma E^{(3)}$, $E^{(4)}$) as well as the non-additivity $\Sigma E^{(n>2)}/\Sigma E^{(2)}$ for the considered three- and four-body models. CIS calculations were carried out using the basis set $6-311++G(3df,3dp)$ at the optimized geometries given in Table 1. All energies are given in eV.

	ΔE	$\Sigma E^{(2)}$	$\Sigma E^{(3)}$	$E^{(4)}$	$\Sigma E^{(n>2)}/\Sigma E^{(2)}$
HeNeHe	−0.4979	−0.5768	0.0789	–	−0.1368
HeHeNe	−0.2993	−0.1850	−0.1143	–	0.6178
HeNeHeNe	−7.8310	−0.8435	0.3401	−7.3276	8.6871
HeNeNeHe	−0.5088	−0.8517	0.2258	0.117	−0.1374
NeHeHeNe	−0.3047	−0.4734	−0.2286	0.3973	−0.8392
$\begin{pmatrix} \mathrm{He} & — & \mathrm{Ne} \\ \vert & & \vert \\ \mathrm{Ne} & — & \mathrm{He} \end{pmatrix}$	−0.5415	−1.2789	−0.8571	1.5945	−1.2468
$\begin{pmatrix} \mathrm{Ne} & — & \mathrm{Ne} \\ \vert & & \vert \\ \mathrm{He} & — & \mathrm{He} \end{pmatrix}$	−8.0242	−0.9531	0.9387	−8.009	8.4031

Table 4. Singlet excited-state total interaction energies ΔE, two-, three, and four-body terms ($\Sigma E^{(2)}$, $\Sigma E^{(3)}$, $E^{(4)}$) as well as the non-additivity $\Sigma E^{(n>2)}/\Sigma E^{(2)}$ for the considered three- and four-body models. CIS calculations were carried out using the basis set $6-311++G(3df,3dp)$ at the optimized geometries given in Table 1. All energies are given in eV.

	ΔE	$\Sigma E^{(2)}$	$\Sigma E^{(3)}$	$E^{(4)}$	$\Sigma E^{(n>2)}/\Sigma E^{(2)}$
HeNeHe	−0.9911	−1.1487	0.1576	–	−0.1372
HeHeNe	−0.6002	−0.3704	−0.2298	–	0.6204
HeNeHeNe	−15.6588	−1.6816	0.6774	−14.6547	8.7147
HeNeNeHe	−1.0091	−1.6959	0.4516	0.2352	−0.1387
NeHeHeNe	−0.6098	−0.9475	−0.4572	0.7948	−0.8388
$\begin{pmatrix} \mathrm{He} & — & \mathrm{Ne} \\ \vert & & \vert \\ \mathrm{Ne} & — & \mathrm{He} \end{pmatrix}$	−1.0739	−2.5524	0.8577	0.6207	−0.2432
$\begin{pmatrix} \mathrm{Ne} & — & \mathrm{Ne} \\ \vert & & \vert \\ \mathrm{He} & — & \mathrm{He} \end{pmatrix}$	−16.041	−1.8942	1.8707	−16.0175	8.4561

contribution to the repulsion. As shown, the pairwise additive terms always contribute to the attraction between the atoms in their ground and excited electronic states, while the non-pairwise additive corrections were either attractive or repulsive.

While the non-pairwise additive contributions were by no means negligible in the ground and excited states of the four-body models, they were significantly smaller than the two-body terms of the three-body models. Fortunately, the least significant contributions of non-additivity were assigned to the $(\mathrm{HeNeHe})_r^*$ intermediate complexes in both the ground and exited states. Since the reactants $\mathrm{He}_2^m(a^3\Sigma_u^+)$ and Ne have been nominated as candidates for a laser active system involving the $(\mathrm{HeNeHe})_r^*$ intermediate, it looks feasible to construct model potentials and simulate larger systems.

4 Conclusions

In the present paper, an attempt has been made to report on *ab initio* calculations performed on two-, three- and four-atomic rare-gas clusters with the purposes of elucidating the mechanism of the population inversion in the He-Ne laser and estimating the importance of two-, three- and four-body terms in the potential of the clusters. Taking into account the reported limitations that affect the accuracy of the calculated energies and assuming Franck-Condon transitions, two major conclusions may be drawn from this work. Firstly, no theoretical evidence was found for the production of neon excited-state complexes other than 20.0858 eV to 20.4875 eV and energy transfer is most probable through the $(\mathrm{HeNeHe})_r^*$ intermediate. Secondly, the non-additive contribution to the total interaction energy of $(\mathrm{HeNeHe})_r^*$ was quite negligible, suggesting that the total interaction energy could be well represented as the sum of the two-body terms. Constructing model potentials and simulation of larger systems may therefore be suggested for future investigations of laser active systems.

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