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Test study on the excitation spectra of the N_2–He van der Waals molecule

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Abstract. We have performed ab initio fourth-order Møller–Plesset perturbation theory calculations in the framework of the supermolecule approach on the vertical excitation spectra of the weakly bound van der Waals N_2–He dimer. They indicate a "T-shaped" stablest ground $N_2(X^1\Sigma_g{}^+)$–He(^{1}S) electronic state with a well depth, D_e, of 21.63 cm^{-1} at a minimum distance, R_e, of 3.44 Å and zero-point vibration correction, D_o, of 7.07 cm^{-1}. They also indicate a "T-shaped" stablest excited conformer with $R_e = 3.25$ Å, $D_e = 36.85$ cm^{-1} and $D_o = 17.06$ cm^{-1} for the $N_2(B^3\Pi_g)$–He(^{1}S) triplet electronic level. In order to investigate the use of less-demanding correlation methods, test density functional theory calculations using the mPW1PW exchange–correlation functional are also presented for comparison.

Keywords: van der Waals molecules – Ab initio calculations – Møller–Plesset perturbation theory – Excitation spectra – mPW1PW exchange–correlation functional

Introduction

Recent advances in the determination of reliable interaction energy (IE) surfaces of van der Waals (vdW) molecules have benefited from highly sophisticated molecular beam techniques and the implementation of high-resolution laser-based spectroscopic experiments [1, 2, 3, 4]. Accurate surfaces are now known for the vdW interaction among rare gases [5] and between H_2 and rare gases [6]. The N_2–rare gas vdW interaction has received a similar amount of attention, since this system constitutes a good prototype for more complex molecular species interacting with rare gases. As N_2–He is the simplest complex to study, it has become a benchmark system for dynamic properties of the gaseous state of the mixture [7]. Since it is the major component of the earth's atmosphere, knowledge of N_2 interacting in various gaseous media is important for an understanding of phenomena such as auroras and airglows.

The availability of powerful computers and the development of efficient computational algorithms have made possible the quantum mechanical study of vdW interactions of small to medium-size molecules [8, 9]. There are two main methods for the ab initio calculation of vdW interactions. The first regards the interaction between the subsystems as a perturbation and partitions the energy into terms such as electrostatic, repulsion, polarization, induction and dispersion. The second approach considers the interacting subsystems as a supermolecule [10, 11]. Since all the highly effective ab initio methods developed for single-molecule calculations are in principle applicable without change, we use the supermolecule approach at present.

Recent developments in nonlinear optics have provided tunable and coherent vacuum UV radiation to obtain high-resolution fluorescence electronic excitation spectra. This technique, combined with supersonic beam expansion techniques to form cold vdW molecules, has been shown to be a powerful tool for studying interatomic potentials of electronically excited rare gas vdW dimers, but the application of these combined techniques to study the intermolecular interaction for N_2–He in its excited electronic states has not been reported so far. There was, nevertheless, an experimental study on the cross-sections for rotationally inelastic collisions of $N_2(B^3\Pi_g)$ with Ar [12].

In the present study we are able to describe the vertical excitation electronic spectra of the diatomic van der Waals N_2–He molecule, in its "T shape" stablest ground-state and excited-state structure [13, 14], using standard perturbation methods of quantum chemistry.

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Despite many technical difficulties, ab initio methods offer a sound basis for the calculation of vdW potential-energy surfaces valid over the whole range of molecular distances and orientations.

Theoretical method

The interaction potential was obtained in the framework of the supermolecule approach at the Hartree–Fock self-consistent-field (HF-SCF) and Møller–Plesset perturbation theory (MP) levels of approximation for the total energy

$$E = E^{\mathrm{HF-SCF}} + E^{\mathrm{MP}}, \tag{1}$$

where the correlation energy is split into contributions that are due to different orders of perturbation:

$$E^{\mathrm{MP}} = E^{\mathrm{MP2}} + E^{\mathrm{MP3}} + E^{\mathrm{MP4}}. \tag{2}$$

The IE has been defined as

$$\mathrm{IE}(\mathbf{R}) = E(\mathrm{N_2{-}He};\mathbf{R}) - E(\mathrm{N_2} - X;\mathbf{R}) - E(X - \mathrm{He};\mathbf{R}), \tag{3}$$

where $E(\mathrm{N_2}–X;\ \mathbf{R})$ and $E(X–\mathrm{He};\ \mathbf{R})$ are used to indicate that the monomer energies are derived in the dimer-centered basis set (DCBS). This amounts to applying the counterpoise procedure of Boys and Bernardi [15] to correct for the basis set superposition error (BSSE), at both the HF-SCF and the correlation levels of approximation at each molecular configuration **R**. Despite the long-lasting controversy on its credibility, the function counterpoise method of Boys and Bernardi proves to be the correct approach [16]. Through fourth order in the correlation perturbation, the IE in Eq. (3) can be expressed through fourth order in the perturbation at any particular geometrical configuration **R**:

$$\mathrm{IE}^{\mathrm{MP(4)}} = \mathrm{IE}^{\mathrm{HF-SCF}} + \mathrm{IE}^{\mathrm{MP2}} + \mathrm{IE}^{\mathrm{MP3}} + \mathrm{IE}^{\mathrm{MP4}}. \tag{4}$$

Currently, going beyond the full fourth-order MP treatment does not seem feasible. It has also been shown that in order to obtain quantitatively meaningful results incomplete higher-order MP calculations must be avoided [17]; thus, the complete fourth-order MP approximation was adopted in the present study. With the linked cluster theorem automatically satisfied for each order of perturbation and this MP scheme being size-consistent [18], it represents one of the best and more economical methods available for reliable calculation of IEs within the supermolecule approach. It also has several advantages compared to other methods owing to its uniform and systematic treatment of the electron correlation contributions [19].

The basis set used for N in the present contribution is based on the medium-sized [10.6.4/5.3.2] Gaussian-type orbital (GTO) one-particle basis set of contracted GTO (CGTO) functions devised by Sadlej [20] (POL basis set), which accounts for the diffuseness of the valence part of the wave function, leads to the correct calculation of intermolecular electrostatic forces and to a negligible secondary BSSE [21]. For He we used the [10.2/5.2] GTO/CGTO basis described by Garrison et al. [22] (referred to as the GLS basis set in the present study) that is designed to describe the He polarizability accurately. They were complemented with a set of bond functions (BFs) taken from Tao and Pan [23]: 3s ($\alpha = 0.9, 0.3, 0.1$), 3p ($\alpha = 0.9, 0.3, 0.1$), 2d ($\alpha = 0.6, 0.2$), 1f ($\alpha = 0.3$). The BFs were placed at the midpoint of the vector **R**, which joins He with the center of mass of $\mathrm{N_2}$. A recent report on the use of BFs and related problems was made by Tao [24].

The necessary energies were calculated using the Gaussian 98 molecular package [25] for the Gaussian integrals, HF eigenvectors and energies, molecular properties, four-index molecular integral transformation and MP calculations.

Results and discussion

Ground $N_2\ (X^1\Sigma_g^+)–He(^1S)$ *state*

High-level ab initio calculations, in the framework of the supermolecule approach, were performed to determine the conformational structure of the $\mathrm{N_2}$–He vdW dimer in its ground electronic state at the restricted HF-SCF and fourth-order MP levels of approximation [18, 19] for the total energy. The IE through fourth order in MP is obtained as

$$\mathrm{IE}^{\mathrm{MP(4)}} = \mathrm{IE}^{\mathrm{RHF-SCF}} + \mathrm{IE}^{\mathrm{MP2}} + \mathrm{IE}^{\mathrm{MP3}} + \mathrm{IE}^{\mathrm{MP4}}. \tag{5}$$

The final MP(4) counterpoise-corrected IEs were computed according to Eq. (5) for all possible configurations of $\mathrm{N_2}$ and He. In the supermolecule calculations, $\mathrm{N_2}$ was kept rigid at its experimental equilibrium bond length of $2.068a_0$. The dimer geometry is specified by **R**, which represents the distance between the center of mass of $\mathrm{N_2}$ and He, and by the polar angle of orientation, β, of the vector along the $\mathrm{N_2}$ bond with respect to the vector along R. The equilibrium bond distance, R_e, and well depth, D_e, are obtained by fitting the calculated fully ab initio MP IE points to an eighth-order polynomial in the stretching coordinate R, analytically continued with a seventh-order polynomial on $1/R$ (from $1/R^6$ to $1/R^{12}$) in the asymptotic $R \to \infty$ region.

The computed minimum IE curve for the ground state of $\mathrm{N_2}$–He is depicted in Fig. 1, which shows how D_e changes with β as compared to recent results from Hu and Thakkar [13]. This figure shows the T-shaped structure to be the stablest configuration, with a D_e of 21.63 $\mathrm{cm^{-1}}$ at an R_e of 3.44 Å for the present calculation, in close agreement with a D_e value of 20.82 $\mathrm{cm^{-1}}$ at an R_e value of 3.43 Å as found by Hu and Thakkar [13] for the same geometry. These values are also in good agreement with previous empirical or semiempirical calculations by Beneventi et al. [14].

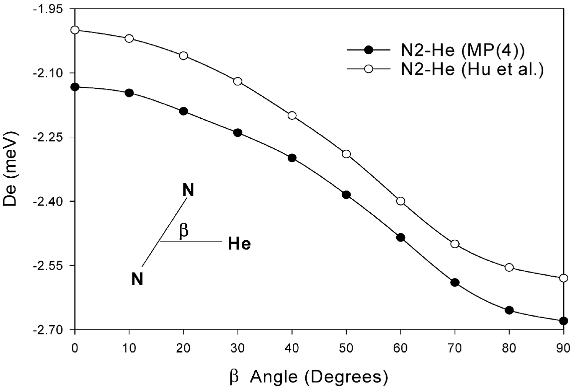

Fig. 1. Angular dependence of D_e for the ground $\mathrm{N_2}(X^1\Sigma_g^+)$–$\mathrm{He}(^1S)$ electronic state

Excited $N_2(B^3\Pi_g)$–$He(^1S)$ states

We have considered the excited $N_2(B^3\Pi_g)$–$He(^1S)$ $\rightarrow$ $N_2(X^1\Sigma_g^+)$–$He(^1S)$ transition as our first choice in the present study for the following reasons:

1. The $B^3\Pi \rightarrow X^1\Sigma_g^+$ transitions in N_2 are well known experimentally.
2. Although there are studies on the $N_2(X^1\Sigma_g^+)$–$He(^1S)$ ground-state system [13, 14], there is only indirect evidence for the formation of the excited $N_2(B^3\Pi_g)$–$He(^1S)$ complex.

High-level ab initio calculations in the framework of the supermolecule approach were performed to determine the interaction of $N_2(B^3\Pi_g)$ with $He(^1S)$ at the unrestricted HF-SCF and the fourth-order unrestricted MP level of approximation (UMP) for the total energy. The IE through fourth order in UMP is then obtained as

$$\mathrm{IE}^{\mathrm{UMP}(4)} = \mathrm{IE}^{\mathrm{UHF-SCF}} + \mathrm{IE}^{\mathrm{UMP2}} + \mathrm{IE}^{\mathrm{UMP3}} + \mathrm{IE}^{\mathrm{UMP4}}. \quad (6)$$

Ab initio calculations of open-shell vdW complexes have been traditionally accomplished using multideterminant wave function methods, which in general impose severe demands on the computational resources (in time and storage). UMP represents an alternative size-consistent economical method available for reliable calculation of IEs [26, 27, 28]. The necessary UMP correlation energies are all calculated by means of the Gaussian 98 molecular package [25] using the basis set described in the previous section. Geometry optimizations were carried out with respect to the intermolecular parameter R for all three conformers with $\beta = 0$, 45 and 90°, respectively.

In contrast to the closed-shell MP procedure, the counterpoise open-shell calculations reported in this section cause additional complications. The valence electron configuration of N_2 in its first $^3\Pi$ electronic excited state corresponds to $(1\pi_u)^4$ $(3\sigma_g)^1$ $(1\pi_g^*)^1$. The degeneracy of the $1\pi_g^*$ orbital is removed by the He atom for any nonlinear conformer of the molecular vdW complex, giving rise to the A′ and A″ (in C_s symmetry) states, respectively [29]. The ^{3}A′ state corresponds to a configuration where the electron is occupying a $1\pi_g^*$ orbital located "parallel" to the N–N–He plane. In the ^{3}A″ state, the electron is occupying a $1\pi_g^*$ orbital located "perpendicular" to the N–N–He plane. All the calculations reported in the present contribution are based on the Born–Oppenheimer approximation and provide adiabatic interactions for the A′ and A″ states. Spectroscopy experiments do not probe such states because one has to account additionally for the spin–orbit coupling, which leads to interaction among the previously mentioned adiabatic states. In this particular case, a proper formalism for bound states accessible in spectroscopy has been set forth by Dubernet et al. [30] in the atom–diatom case, where the diabatic interaction can be represented as the average of the A′ and A″ interaction potentials. In the present contribution we have represented the $N_2(B^3\Pi_g)$–$He(^1S)$ interaction potential on N_2–He as the average among the corresponding $N_2(^3A')$–$He(^1S)$ and $N_2(^3A'')$–$He(^1S)$ states.

Another problem related to applying the supermolecular UMP method to open-shell molecular systems is the spin contamination, which has to be small and of about the same magnitude within the N_2–He dimer and the N_2 monomer [26, 31, 32]. In all our calculations the spin contaminations were small, i.e., $< S^2 >$ was equal to 2.02 in the triplet state for both N_2–He and N_2 in the DCBS.

The calculated R_e and D_e values in three different geometries represented by $\beta = 0$, 45 and 90 °, respectively, for the $N_2(B^3\Pi_g)$–$He(^1S)$ electronic state of N_2–He are shown in Table 1. As for the ground state, R_e and D_e were also obtained here by fitting the calculated fully ab initio MP IE points to an eighth-order polynomial in the stretching coordinate R, analytically continued with a seventh-order polynomial on $1/R$ (from $1/R^6$ to $1/R^{12}$) in the asymptotic $R \rightarrow \infty$ region. Table 1 reveals that, at the UMP(4) level of approximation used and for all the states and geometries explored in the present study, the T-shaped structure represents the stablest conformation, followed by the linear conformation, while the least stable geometry is always represented by the structure with $\beta = 45°$.

In order to test the convergence of the perturbation series involved in the previous results, we calculated the IE at the CCSD(T) level of theory for the (R_e, β_e) points already found as the minimum energy points at the MP4 level of approximation. The calculated CCSD(T) IE is only 0.24 cm^{-1} deeper for the ground $N_2(X^1\Sigma_g^+)$–$He(^1S)$ interaction at $R_e = 3.44$ Å and $\beta_e = 90°$. Similarly, the CCSD(T) IE is only 0.18 cm^{-1} less stable for the excited $N_2(B^3\Pi_g)$–$He(^1S)$ interaction at $R_e = 3.25$ Å and $\beta_e = 90°$. These results imply that the inclusion of iterative excitations seems to have a marginal effect upon the $N_2(X^1\Sigma_g^+)$–$He(^1S)$ and $N_2(B^3\Pi_g)$–$He(^1S)$ interactions.

Our final $N_2(X^1\Sigma_g^+)$–$He(^1S)$ $\rightarrow$ $N_2(B^3\Pi_g)$–$He(^1S)$ vertical excitation spectra for N_2–He in its T-shaped ground-state and excited-state configurations is depicted in Fig. 2. Vibrational energies were calculated from the fitted potential curves using the numerical Numerov–Cooley procedure [33] by treating N_2–He as a diatomic system with only one degree of freedom R. This procedure shows that for the ground $N_2(X^1\Sigma_g^+)$–$He(^1S)$ electronic state (lower curve in Fig. 2) the calculated dissociation energy corresponds to a D_o value of 7.07 cm^{-1}, with at least one vibrational state supported by this T structure. The present calculations also show

Table 1. Equilibrium bond distance, R_e, and well depth, D_e, as a function of β (degrees) for $N_2(B^3\Pi_g)$–$He(^1S)$ at the UMP(4)/POL + GLS + BF level of theory

β	R_e (Å)	D_e (cm^{-1})
90°	3.25	36.85
45°	4.05	13.69
0°	3.97	34.46

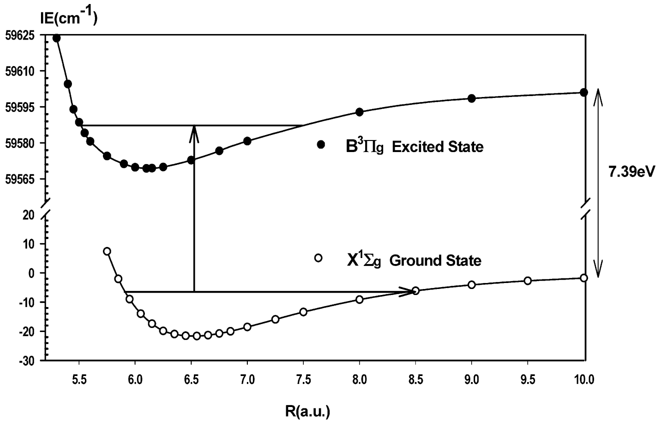

Fig. 2. $N_2(X^1\Sigma_g^+)$–He(^{1}S) → $N_2(B^3\Pi_g)$–He(^{1}S) vertical excitation energies for the T structure of N_2–He

that the minimum of the excited $N_2(B^3\Pi_g)$–He(^{1}S) triplet interactions (upper curve in Fig. 2) occurs at $R_e = 3.25$ Å, $D_e = 36.85$ cm^{-1} and $D_o = 17.06$ cm^{-1}, with only one vibrational state supported by this T-shaped structure. The present calculations also indicate a redshift of 9.99 cm^{-1} for the $N_2(X^1\Sigma_g^+)$–He(^{1}S) → $N_2(B^3\Pi_g)$–He(^{1}S) vertical excitation energy, with respect to the corresponding $N_2(X^1\Sigma_g^+)$ → $N_2(B^3\Pi_g)$ excitation in the absence of He.

In more detail: the excited $N_2(B^3\Pi_g)$–He(^{1}S) triplet interaction minima occur at $R_e = 3.18$ Å and $D_e = 39.89$ cm^{-1} for the "parallel" $N_2(^3A')$–He(^{1}S) state and at $R_e = 3.25$ Å and $D_e = 29.23$ cm^{-1} for the "perpendicular" $N_2(^3A'')$–He(^{1}S) state, the A' level being stabler by 6.91 cm^{-1}. The large A''–A' splitting and relative ordering obtained for the T-shaped structures examined in this study did not change significantly when a more correlated CCSD(T) method was used, which implies that there is indeed a significant variation in the interaction between a N_2 molecule in its electronic $^3\Pi$ excited state and a He atom when the unfilled π^* orbital is parallel or perpendicular to the N–N–He plane. This result is in agreement with experimental results on the cross-sections for rotationally inelastic collisions of $N_2(B^3\Pi_g)$ with Ar [12], where it is argued that the diffuse antibonding $1\pi_g^*$ orbital has a significant effect on the N_2–Ar interaction. The deeper minimum found in connection with $^3A'$ (compared to the $^3A''$ state) in the T-shaped geometry examined in this study also reveals that this region is dominated by the dispersion interaction of He with the N_2 molecule in its electronic $^3\Pi$ excited state, since this attractive interaction will be stronger when the singly filled $1\pi_g^*$ electron lies in the N–N–He plane.

Density functional theory representation of the excited states

In view of the recent successfully reported study on the structure and bonding properties of the ground $N_2(X^1\Sigma_g^+)$–He(^{1}S) electronic state by means of the mPW1PW exchange–correlation functional using density functional theory (DFT) local-spin-optimized atom-centered basis sets complemented with BFs optimized at the mPW1PW level of theory [34], we decided to perform similar test calculations on the excited $N_2(B^3\Pi_g)$–He(^{1}S) electronic states of N_2–He, which are to be compared to the ab initio UMP(4) reference calculations presented already in a previous section. The present excited-state calculations are always possible within DFT since it corresponds to the $^3\Pi$ symmetry level of lowest energy.

DFT calculations were performed in the framework of the supermolecule approach by applying the Kohn–Sham formalism [35], where the IE was defined as given by Eq. (3), i.e., by applying the counterpoise procedure of Boys and Bernardi [15] to correct for the BSSE at each molecular configuration. The mPW1PW [36] exchange–correlation functional was tested as implemented in the Gaussian 98 molecular package [25] for the total energy. In the DFT calculations, we used the TZVP and the DZVP2 atom-centered Gaussian basis set for N and He atoms, respectively, which has been optimized for local spin DFT calculations by Godbout et al. [37]. They were complemented with a basis set taken from the standard BFs recommended by Tao and Pan [23, 24], but were modified to increase the ground-state dispersion energy interaction on N_2–He at the mPW1PW level of theory [34]. These DFT-optimized BFs are referred to here as BF-DFT, and they consist of three s functions (exponents 0.9, 0.3 and 0.1), three p functions (exponents 0.5, 0.3, 0.1), two d functions (exponents 0.4 and 0.2), one f function (exponent 0.4) and one g function (exponent 0.4). The BFs were placed at the midpoint of the vector **R**, which joins He with the center of mass of N_2. Here, we have also represented the $N_2(B^3\Pi_g)$–He(^{1}S) interaction potential as the average among the corresponding $N_2(^3A')$–He(^{1}S) and $N_2(^3A'')$–He(^{1}S) states.

The calculated R_e and D_e values for $\beta = 0$, 45 and 90°, respectively, for the $N_2(B^3\Pi_g)$–He(^{1}S) electronic state of N_2–He at the mPW1PW/TZVP + DZVP2 + BF-DFT level of theory [34] are shown in Table 2. It reveals that at the mPW1PW level of approximation the T-shaped structure represents the stablest conformation, followed by the linear conformation, while the least stable geometry is always represented by the structure with $\beta = 45°$, in agreement with the UMP(4) reference results presented in Table 1. We can also observe relatively close D_e values for $\beta = 45°$, but the rest of the D_e values obtained for different geometries using the mPW1PW1 functional are far from their UMP(4) counterparts. It also shows R_e values systematically larger at the mPW1PW level of theory compared to the present perturbation reference calculations.

Table 2. R_e and D_e as a function of β for $N_2(B^3\Pi_g)$–He(^{1}S) at the mPW1PW/TZVP + DZVP2 + BF-DFT level of theory

β	R_e (Å)	D_e (cm^{-1})
90°	3.62	22.92
45°	4.09	15.02
0°	3.98	21.87

On the whole, the exchange–correlation functional mPW1PW using the ground-state DFT-optimized BFs [34] gives a qualitative representation of the IE of the lowest $^3\Pi$ level of the N_2–He van der Waals dimer, although it still shows more anisotropic behavior, which in turn produces highly stable T and linear structures compared to the UMP(4) reference calculations presented. No further steps were taken to improve these values at the mPW1PW level of theory by optimizing the BFs for the excited state.

Final remarks

Although all points on the calculated IE curves are fully ab initio, the present results are to be taken only as a qualitative guide. Although the ground N_2–He state is very well represented compared with the available ab initio results, this may not necessarily be the case for the excited states examined here. In order to increase the predictive value of Fig. 2, one has to investigate the behavior of the present basis set to represent the electric properties and correlation energy of the excited states involved, using higher-level correlation benchmark calculations as a comparison. Nevertheless, extending the size of the present basis and using highly correlated methods is very difficult to accomplish in practice, mainly because these correlation energy calculations are already extremely demanding on computational resources (processing time and storage). Considering that the long-term goal of the present study is to represent a "complete IE surface" for several excited states of interest, it will be useless to increase the size of the basis sets and use high-quality electron correlation methods. At present, it would be more advisable to investigate the use of less-demanding DFT methods in order to undertake such a challenging task.

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