Intermolecular potential and *ab initio* spectroscopy of the Ne–HF complex

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ABSTRACT

The intermolecular potentials for the Ne–HF complex have been calculated using MP2 and SIMPER-P methods. A detailed analysis of the intermolecular potential is carried out using the perturbation theory. The energies of Van der Waals rovibrational bound states are calculated from the potential energy surfaces, and compared with previously published high-resolution spectra. SIMPER-P method is shown to produce results competitive to high-level CCSD(T) method and to be in good agreement with experimental results.

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1. Introduction

The goal of this work is to investigate the performance of the SIMPER-P method for the calculation of intermolecular potentials and assessment of the accuracy of this technique compared with experiment and other theoretical predictions. This investigation can be considered as the logical continuation of a recent work [1] which addressed the performance of the SIMPER-K method applied to the estimation of the spectroscopic properties of the Ne–HF complex. SIMPER-P method had been used in practice in preference to SIMPER-K and was successfully applied to the calculation of intermolecular potentials and thermodynamic (mixed) second virial coefficients of H_2O-N_2 and H_2O-O_2 complexes [2,3]. Thus, the application of the SIMPER-P method to estimate the spectroscopic properties of the Van der Waals complexes is a valuable test of the efficiency of this method. In this work we calculate the intermolecular potential energy surfaces for the Ne–HF complex using MP2 and CCSD(T) methods. We then apply the systematic intermolecular potential extrapolation routine (SIMPER-P, the symbol 'P' stands for 'perturbative') to the MP2 intermolecular potential. We then carry out the analysis of results based on the components of the total potential and monomer properties. The intermolecular potential estimated on a two-dimensional grid of points is then fitted to a suitable functional form and the set of ro-vibrational bound states is calculated, which is followed by the comparison of the results, obtained in this work with the data coming from previous studies – experimental and theoretical. In the following section we will describe the details of *ab initio* calculations, will give a brief description of the theory standing behind the SIMPER-P, describe the fitting procedure, present and discuss the results.

2. Calculations and results

The intermolecular potential energy surfaces are calculated using MP2 and CCSD(T) supermolecule methods with MOLPRO package [4], applying the full counterpoise correction [5], with the SP-aug-cc-pV5Z basis set [6]. This basis set is believed to be close enough to the complete basis set limit that the different methods can be fairly compared. The MP2 and CCSD(T) calculations are performed in the full core approximation, i.e. allowing the electron transitions from the core orbitals. A polar coordinate system is used. The intermolecular geometries are described by the R and θ coordinates of the Ne bond vector **R** with the F atom located at the origin and F–H bond directed along the positive z axis. R represents the length of the vector **R**, and θ the angle this vector makes with the HF molecule, taking as $\theta = 0$ the Ne–HF configuration. The coordinate system used is shown in Fig. 1. The H–F distance is fixed at its equilibrium value, 1.73291 a_0 [1]. The intermolecular potential energy surfaces are calculated on a grid consisting of 1887 geometries. Calculations are performed at 51 distances with the step size 0.1 Å, and 37 angles, $\Theta = 0(5)180°$. The SIMPER-P method is used to extrapolate the MP2 supermolecule calculations. The same basis set is used for SIMPER-P as for the other calculations.

The starting point of SIMPER-P method consists of splitting the total interaction energy estimated at a low level of theory, which in this work corresponds to Møller–Plesset second-order perturbation theory, in the supermolecule approach into components resembling counterparts from perturbation theory:

$$\Delta E_{\text{tot}}^{\text{low}} = \Delta E_{\text{Coul}}^{\text{low}} + \Delta E_{\text{exch}}^{\text{low}}. \tag{1}$$

Here $\Delta E_{\text{tot}}^{\text{low}}$ is the total interaction energy calculated using the 'low-level' supermolecule method (MP2), with counterpoise correction, and $\Delta E_{\text{Coul}}^{\text{low}}$ is the MP2 Coulomb interaction energy. As a result, the exchange–repulsion energy $\Delta E_{\text{exch}}^{\text{low}}$ is found indirectly from Eq. (1) at each point on the surface. Several alternative methods for

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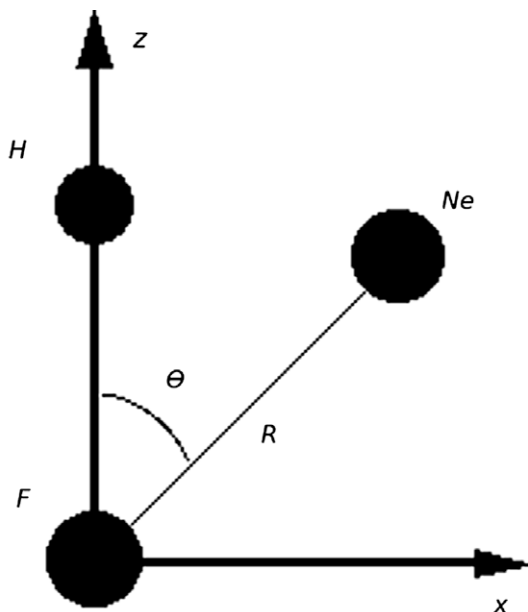
Fig. 1. Coordinate system used in the description of the complex.

calculating the MP2 Coulomb interaction energy have been investigated [7] with the conclusion that the most reliable and efficient method for weak intermolecular forces is SIMPER-P. In the SIMPER-P method, the MP2 Coulomb interaction energy is calculated using Rayleigh–Schrödinger perturbation theory to second order in the interaction. The resulting sum of first-order and second-order terms can be rigorously split into electrostatic, induction and dispersion energy contributions

$$\Delta E_{Coul}^{low} = \Delta E_{elst}^{low} + \Delta E_{ind}^{low} + \Delta E_{disp}^{low}. \tag{2}$$

The aim of the SIMPER-P method is to improve the Coulomb and exchange–repulsion components of the low-level interaction energies using the high-level and low-level monomer properties and the knowledge about the complex set of relationships existing between them, which forms the core of the extrapolation procedure. This procedure would lead to approximate high-level terms which can then be added to give the final intermolecular potential

$$\Delta E_{tot}^{high} = \Delta E_{elst}^{high} + \Delta E_{ind}^{high} + \Delta E_{disp}^{high} + \Delta E_{exch}^{high}. \tag{3}$$

We extrapolate the electrostatic and induction energies to higher-level using accurate CCSD densities. We apply the overlap model combined with the use of CCSD charge densities to extrapolate the exchange–repulsion energy. The dispersion energy is improved by expanding the Uncoupled Hartree–Fock (UCHF) interaction energy, which exactly corresponds to the second-order dispersion energy term of the total MP2 interaction energy, into damped multipolar series and substituting the UCHF dispersion energy coefficients by accurate TD-CISD coefficients calculated in the multipolar approximation from the knowledge of TD-CISD polarizabilities. The induction energy is improved in SIMPER-P by substitution of MP2 monomer densities by accurate CCSD monomer densities in the expression for the second-order MP2 induction energy. The detailed description of methods used in SIMPER-P to calculate each term in Eq. (3) is given in [2].

To obtain a two-dimensional potential energy surface, which is suitable for calculating the rovibrational bound states the dependence of the interaction energy on the angle θ is represented as a series of Legendre polynomials and the radial dependence is represented as a linear combination of intermolecular inverse power distance functions

$$E(R, \theta) = \sum_{\lambda=0}^{\lambda_{max}} \sum_i E_{i\lambda} \frac{P_\lambda(\cos\theta)}{R^i} \tag{4}$$

with $\lambda_{max} = 6$ and $i = 1$–6. The fit to all 1887 energies uses 42 independent parameters and minimizes the Boltzmann weighted error:

$$\Omega^2 = \frac{\sum_g \omega_g^2 \times (E_{fit}(g) - E_{calc}(g))^2}{\sum_g w_g^2} \tag{5}$$

with weights given by

$$\omega_g = e^{-E_{calc}(g)/E_b}, \tag{6}$$

where $E_b = 500 \; \mu E_h$ and $1 \; m \; E_h \approx 4.35974 \times 10^{-18}$ J. The best fit gives $\Omega \approx 0.43 \; \mu E_h$.

The parameters of the intermolecular potential can be obtained from the author on request.

The contour plot of the intermolecular potential is shown in Fig. 2. As in previous studies we observe two minima corresponding to Ne–H–F (global) and Ne–F–H (local) orientations and a transition state in a roughly T-shaped geometry. The well depths and equilibrium separations at the linear Ne–H–F minimum and Ne–F–H secondary minimum are compared with the best 'morphed' potential of Meuwly and Hutson [8] in Table 1. The angular dependence of the distance optimized potentials is shown in Fig. 3. As can be seen from the results shown in Table 1 and Fig. 3, SIMPER-P tends to slightly overestimate, while the MP2 method tends to considerably underestimate the interaction energies compared to CCSD(T) method and experimental results.

To facilitate the analysis we present in Table 2 the components of the total MP2 (low-level) and SIMPER-P (extrapolated to a high-level) potentials at different angles and intermolecular distances corresponding to minima. The binding at the Ne–H–F minimum is dominated by both dispersion and induction energies. Binding at the Ne–F–H minimum is dominated by dispersion interaction. As it is shown in Table 2 the total interaction energies at the minima are governed by a fine balance between attractive and repulsive terms. In order to explain the effect produced by SIMPER-P
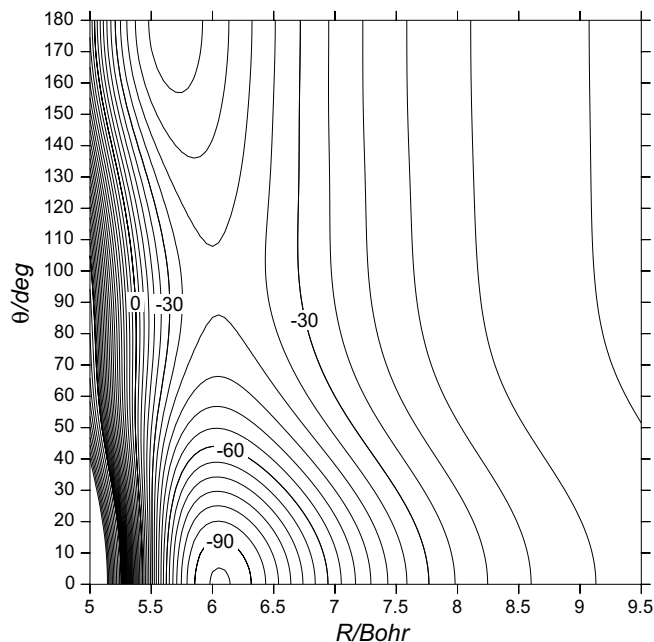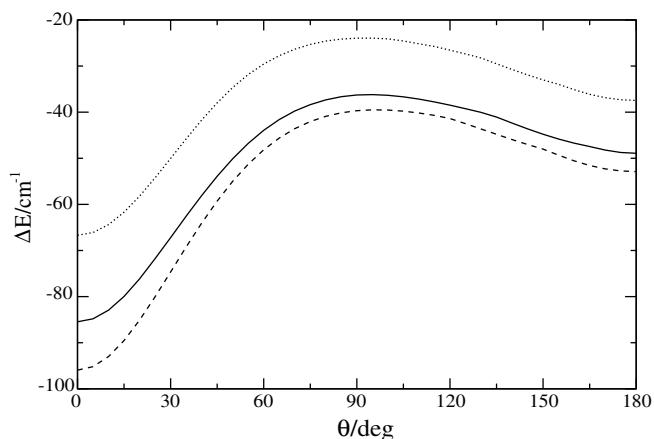

Fig. 2. Contour plot in Jacobi coordinates of the sp-aug-cc-pV5Z SIMPER-P intermolecular potential energy surface fitted by the analytic function. The successive contours are spaced by 5 cm^{-1}.

Table 1
Minima of the potential energy surface for Ne–HF complex.

Method	Configuration R_e (a_0)/ΔE (cm^{-1})	
	Ne–HF	Ne–FH
MP2	6.27/−66.7	5.87/−37.5
SIMPER-K [1]	6.08/−93.7	5.67/−53.0
SIMPER-P	6.06/−95.8	5.67/−52.8
CCSD(T)	6.15/−86.0	5.74/−49.1
MH [8]	6.19/−88.5	5.70/−50.0

Table 3
Calculated and experimental values of Ne and HF dipole–dipole polarizabilities.

HF		Ne	
Property	Value (a.u.)	Property	Value (a.u.)
α_{UCHF}	4.088	α_{UCHF}	1.967
α_{SCF}	4.910	α_{SCF}	2.363
α_{MP2}	5.653	α_{MP2}	2.680
α_{CISD}	5.332	α_{CISD}	2.579
α_{EXP} [11]	5.520	α_{EXP} [12]	2.662

Fig. 3. Angular dependence of the distance optimized Ne–HF potential. Solid line – CCSD(T), dashed line – SIMPER, dotted line – MP2.

methodology applied to the MP2 intermolecular potential we compare the monomer properties, namely isotropic dipole–dipole polarizabilities of Ne and HF molecules, which are shown in Table 3. Polarizabilities are calculated at different levels of theory. Keeping in mind the hierarchy of *ab initio* methods we expect that CCSD(T) polarizabilities would be closest to experimental values. We assume that the 'CCSD molecule' is more 'compact' compared to 'MP2 molecule', i.e. the electronic charge density is less extended in space and the ionization potentials are usually higher, increasing the chemical hardness, or, alternatively, decreasing polarizability [9], which is shown in Table 3. We believe that this fact may serve as an explanation of the lowering of absolute values of the high-level exchange–repulsion, electrostatic and induction energies in the regions close to the minima. Within the same line of arguments we explain the increase of the absolute values of the high-level dispersion energy term by comparing CISD and UCHF dipole–dipole polarizabilities of monomers. Thus, UCHF method tends to underestimate the polarizabilities of the monomers by 26%, which is reflected in the differences of the high-level and low-level dispersion energies. We see another possible source of the deviation of the SIMPER-P interaction energies from the true values in the use of MP2 response functions in the calculation of the high-level second-order induction energies. Thus, comparing the experimental and MP2 values of polarizabilities, we observe that the MP2 method overestimates the polarizabilities by 2%.

Although we achieved slight improvements in calculation of the high-level induction energies by using accurate CCSD densities in the present version of SIMPER-P, we believe that the use of the CCSD response functions or the partial modification of MP2 response functions in calculations of high-level interaction energies will lower the absolute values of the induction energies leading to lowering of absolute values of the total potential. We must also note that in present version of SIMPER-P the overlap parameter is kept independent from the level of theory and is only the function of intermolecular coordinates. The recent study by Heßelmann and Jansen [10] addressing the effect of the intramolecular correlation on intermolecular first-order exchange–repulsion energies has shown that there is only 1% difference between the MP2 and CCSD first-order exchange–repulsion energies for the Ne–HF dimer in the region of the global minimum. Although, our intermolecular exchange–repulsion energy term does not exactly correspond to the term described in [10], we believe that considering the dependence of the overlap parameter on the level of theory will lead to the optimal balance between the terms of the total interaction energy and the most accurate extrapolation. The work in this direction is currently underway in our group.

We used the SIMPER-P intermolecular potential energy surface to calculate the rovibrational spectra of the Ne–HF and Ne–DF complexes. Bound states for the SIMPER-P potential are calculated using the program BOUND [13]. Nine rotational functions, from $J = 0$ to $J = 8$, are included in the angular expansion of the rovibrational wavefunctions, with rotational constants of 19.787478 cm^{-1} for Ne–HF and 10.564179 cm^{-1} for Ne–DF. The reduced masses are 9.999665 u for Ne–HF and 10.24489 u for Ne–DF. The radial wavefunctions are propagated between 4 and 20 a_0, and the step size used in the calculations is $10^{-4} a_0$, with a convergence limit tolerance of 10^{-4}.

The calculated transition wavenumbers are compared in Table 4 with experimental values and existing theoretical predictions. The Ne–HF complex has one excited Van der Waals vibrational state, the Π bend. The Ne–DF complex also has a Σ stretch and a Σ bend. The parameter $\Delta = (-E_2 + 3E_1 - 2E_0)/24$ is sensitive to the radial curvature of the potential around the minimum.

In agreement with the comparative analysis of the intermolecular potential energy surfaces the results of the calculation of bound states confirmed the fact that SIMPER-P slightly overestimates the binding. This is illustrated by comparison of the rotational constants, which are roughly equal to half the differences of the transition wavenumbers listed in Table 4.

Table 2
Components of the intermolecular potential (cm^{-1}) in the vicinity of the Ne–H–F ($\theta = 0$) and Ne–F–H ($\theta = 180$) minima, obtained with the SP-AV5Z basis set. The angle θ is given in degrees and R is in atomic units.

R/θ	ΔE_{es}^{low}	ΔE_{es}^{high}	ΔE_{ind}^{low}	ΔE_{ind}^{high}	ΔE_{disp}^{low}	ΔE_{disp}^{high}	ΔE_{exc}^{low}	ΔE_{exc}^{high}
6.047/0.0	−42.8	−39.5	−93.0	−91.9	−120.8	−144.8	194.5	180.2
6.047/100.0	−17.6	−15.5	−7.4	−7.5	−61.8	−74.1	65.1	57.6
5.669/180.0	−19.0	−17.3	−6.7	−6.8	−85.0	−97.7	75.2	68.8

Table 4
Comparison of transition wavenumbers of Ne–HF and Ne–DF, calculated using four *ab initio* potentials and the morphed MH potential [8], with experimental values [1].

Transition	Exp.	MH	SIMPER-P	SIMPER-K [1]	MP2 [1]	CCSD(T) [1]
Ne–HF						
Binding energy D_0		32.830	34.538	32.683	18.409	28.898
v=0: $E_1 - E_0$	0.2989	0.2997	0.3095	0.3003	0.2706	0.2916
$\Delta \times 10^5$	1.97	1.954	1.942	2.023	2.972	2.160
Π bend: $E_{1f} - E_0$	44.0340	44.0716	44.6885	44.4898	–	43.9214
$E_{2f} - E_{1f}$	0.5938	0.5936	0.6095	0.5974	–	0.5795
$E_{1e} - E_{1f}$	0.02058	0.0194762	0.021025	0.0285614	–	0.0171194
Ne–DF						
Binding energy D_0	35.1	35.009	37.189	35.018	19.523	30.911
v=0: $E_1 - E_0$	0.2961	0.2959	0.3071	0.2907	0.2642	0.2829
$\Delta \times 10^5$	1.608	1.66	1.652	1.647	2.551	1.782
Σ bend: $E_0 - E_0$	19.5295	19.538	19.8001	19.2978	15.0181	19.2291
$E_{J=1} - E_{J=0}$	0.2689	0.2689	0.2774	0.2949	0.1896	0.2844
Σ stretch: $E_0 - E_0$	23.3811	23.3809	25.1794	23.4722	17.9296	21.3463
$E_1 - E_0$	0.2382	0.2377	0.245	0.2262	0.2575	0.2155
Π bend: $E_{1f} - E_0$	27.2791	27.2533	28.2994	27.934	–	27.0403
$E_{2f} - E_{1f}$	0.5830	0.5823	0.5986	0.5836	–	0.5662
$E_{1e} - E_{1f}$	0.02298	0.0232908	0.02458	0.018972	–	0.0194825

3. Conclusion

The intermolecular potentials for the Ne–HF complex have been calculated using MP2, CCSD(T) and SIMPER-P methods. The topology of the intermolecular potentials was investigated. Two minima were located corresponding to the linear Ne–HF configuration (global minimum) and Ne-FH configuration (local minimum). A detailed analysis of the MP2 and SIMPER-P intermolecular potentials was carried out using perturbation theory. It is shown that the dispersion energy is the dominant component responsible for binding in the regions of global (Ne–HF) and local (Ne–F–H configuration) minima. Comparative analysis of the intermolecular potentials has shown that MP2 method considerably underestimates the binding, while the global and local minima of the SIMPER-P intermolecular potential energy surface are close to the minima of the CCSD(T) intermolecular potential energy surface, used as a benchmark in this work, but are slightly lower. These observations were confirmed by the results of the calculation of rovibrational bound states of the Ne–HF and Ne–DF complexes. In order to investigate the possible sources of the overestimation of the binding energies by SIMPER-P method we compared the components of the total interaction energy calculated at the low level of theory (MP2) and the high level (SIMPER-P). We arrived to the conclusion that the use of the CCSD response functions in the calculation of the high-level induction energies is expected to lower their absolute values. We believe that considering the dependence of the overlap parameter on the level of theory will lead to the optimal balance between the terms of the extrapolated total interaction energy. The work in this direction is currently underway in our group.

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