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Theoretical study on the interaction potential and bound states of the Ne-BeH complex

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Abstract. The first two-dimensional potential energy surface for the Ne-BeH van der Waals interaction is calculated by the single and double excitation coupled-cluster theory with noniterative treatment of triple excitations [CCSD(T)]. Mixed basis sets, aug-cc-pVQZ for the Be , H and Ne atom, with an additional $(3s3p2d1f1g)$ set of midbond functions are used. There is a single global minimum at $R_e = 6.95a_0$ and $\theta_e = 72.5^\circ$ with well depth -34.43607 cm^{-1}. Based on the potential, the rovibrational energy level structure of the Ne-BeH complex is also investigated.

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Key words: molecular spectroscopy, van der Walls, CCSD(T), bound states

1 Introduction

The nonbonding interaction potential, mainly resulted from van der Waals (vdW) interaction, plays a crucial role to understand the structures and properties of gases, liquids, solids, as well as any other in condensed phase. In the past several decades, there were a lot of experimental and theoretical studies for the closed-shell and open-shell vdW systems [1–6].

Recent progress in the development of experimental methods for the cooling and trapping of atoms and molecules may provide an opportunity for high resolution spectroscopy, accurate determination of intermolecular potential, and the study of reactive and inelastic collision at ultralow temperature [7,8]. Several methods have been proposed for creating translationally cold molecules. A successful demonstration of trapping CaH in a magnetic trap was carried out by Doyle and co-workers [9]. A cold buffer gas of ^{3}He was used to cool molecules to a temperature of about 240 mK. Molecules, slowed down by elastic collisions with the buffer gas, were further trapped in an inhomogeneous magnetic field. The open-shell molecule is paramagnetic molecules and hence suitable for the magnetic trapping from viewpoint of experiment.

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In 2003, Groenenboom and Balakrishnan [2] reported the interaction potential of the He-CaH vdW complex for the first time. The calculation was performed by RCCSD(T) and supermolecule approach. The interaction energy for 3732 geometries was analytically fitted to a three-dimensional potential model. In the accompanying paper [10], they reported quantum scattering calculations of rovibrational transitions in CaH induced by collisions with 3He atom over a wide range of temperatures and compared the data with the experimental results of Doyle and co-workers.

To our knowledge, there is no theoretical and experimental study on the structures and dynamics of the Ne-BeH complex. In this paper, we report the two-dimensional interaction potential of the Ne-BeH vdW complex using CCSD(T) method and big basis set extended with an additional ($3s3p2d1f1g$) set of midbond functions. The rovibrational energy level structure of the Ne-BeH complex is also investigated based on the potential.

2 Computational details

Jacobi coordinates are used throughout the present work. In these coordinates, r_{BeH} is the BeH bond length, R refers to the distance between the Ne atom and the center of mass of BeH molecule, and θ is the angle between R and r_{BeH} with $\theta = 0°$ referring to the Ne-H-Be linear configuration.

2.1 Ab initio calculation

The interaction potential energy surface of the Ne-BeH complex is calculated by the single and double excitation coupled-cluster theory with noniterative perturbational treatment of triple excitations [CCSD(T)] [11–13]. We employ the augmented correlation-consistent polarized valence quadruple zeta (aug-cc-pVQZ) basis set for the H ,Be and Ne atom with the additional set of ($3s3p2d1f1g$) midbond functions (denoted by BF) centered in the middle of the van der Waals bond. The midbond functions are well known to improve the basis set convergence very efficiently. The exponents of these midbond functions are 0.90, 0.30, 0.10 for the $3s$ and $3p$ functions, 0.60, 0.20 for the $2d$ functions, and 0.30 for the $1f$ and $1g$ functions [14]. We denote this basis set as avqz +33211. It is found if the avqz +33211 basis set is used directly the calculation will encounter the convergence problem in the step of CCSD(T) computation of complex. In order to overcome this difficulty, we firstly perform Hartree-Fock calculation using a small basis set, the cc-pVDZ for the H and Be atom and the cc-pVTZ for the Ne atom, and save the orbit. In the second step we then use the saved orbit as the initial guess orbit in the following calculation with avqz +33211 basis set.

The supermolecule approach is adopted to get the intermolecular potential energy for each configuration. The full function counterpoise method of Boys-Bernardi [15] is invoked to correct for the basis set superposition error (BSSE). Calculations are performed over 19 values of the intermolecular separation R: $\{5.0,5.5,6.0,6.5,7.0,7.5,8.0,8.5,9.0,10.0,11.0,12.0,13.0,15.0,17.0,19.0,22.0,25.0,30.0\}$ a_0, and over 12 angles θ

$\{0,20,40,60,70,80,90,110,130,150,170,180\}^\circ$, resulting in a potential energy surface consisting of a total of 228 configurations. In the calculations the BeH bond length is fixed at the determined equilibrium value of $2.538092a_0$. The CCSD(T) calculations are performed using MOLPRO 2006 package [16].

2.2 Fitting procedure

In order to facilitate the following application of the calculation for the energy level structure, the *ab initio* grid-point values are fitted to a two-dimensional potential model proposed by Bukowski *et al.* [17] and used by other researchers [18,19]. The model potential function is the sum of the short-range term V_{sh} and the asymptotic term V_{as}

$$V(R,\theta)=V_{sh}(R,\theta)+V_{as}(R,\theta), \tag{1}$$

where

$$V_{sh}(R,\theta)=G(R,\theta)e^{B(\theta)-D(\theta)R}, \tag{2}$$

$$V_{as}(R,\theta)=\sum_{n=6}^{9}\sum_{\substack{l=0,2,\cdots\\ l=1,3,\cdots}}^{n-4} f_n(B(\theta))\times\frac{C_{nl}}{R^n}P_l^0(\cos\theta), \tag{3}$$

$D(\theta)$,$B(\theta)$ and $G(R,\theta)$ are all expansions in Legendre polynomials $P_l(\cos\theta)$

$$B(\theta)=\sum_{l=0}^{5}b_lP_l^0(\cos\theta), \tag{4}$$

$$D(\theta)=\sum_{l=0}^{5}d_lP_l^0(\cos\theta), \tag{5}$$

$$G(R,\theta)=\sum_{l=0}^{5}(g_{0l}+g_{1l}R+g_{2l}R^2+g_{3l}R^3)P_l^0(\cos\theta). \tag{6}$$

The $f_n(x)$ in Eq. (3) is the Tang-Toennies damping function [20]

$$f_n(x)=1-e^{-x}\sum_{k=0}^{n}\frac{x^k}{k!}, \tag{7}$$

b_l,d_l,g_{kl} and C_{nl} are all adjustable parameters.

In order to obtain a reliable fit, in particular for the long-range part of the potential, a two-step linear least squares fit procedure is employed [19,21]. The $n=6$ and 7 terms of the long-range function V_{as} are first fitted by the *ab initio* values with $R\geq 11a_0$. After then, the long-range coefficients for $n=6$ are fixed, and all other parameters including the $n=7$, 8 and 9 long-range coefficients are determined. The global RMS error of the fit is 0.0305 cm^{-1}

and the maximum absolute error is 0.0467 cm^{-1} for all grid-points. In the vicinity of the potential well, the relative error is less than 0.15%. In the long-range the relative error is within 1.4%. Table 1 lists all the fitted coefficients. A FORTRAN subroutine for generating the two-dimensional PES is available upon request.

Table 1: Coefficients of the analytical PES fitted to the avqz +33211 value of interaction energies.

	$l=0$	$l=1$	$l=2$	$l=3$	$l=4$	$l=5$
b	12.369167	0.6158338	1.4700104	0.12792201	-0.21486130	0.094880485
d	-1.818094	-0.0028047	-0.1740324	0.02076570	0.04.017640	-0.01111877
g_0	-0.5099008	0.5448026	0.20550488	-0.07761225	-0.28194775	0.077833933
g_1	-0.6673928	1.6480530	0.3626818	0.16952491	-0.80666714	0.20892319
g_2	3.4390314	2.5322831	-0.9564020	2.2433956	-1.0996734	0.23792252
g_3	-0.04936727	-0.9268616	0.8307578	-0.52512171	0.24063640	-0.08792296
$C_{60}=-5.7590584\times10^{6}$,	$C_{62}=6.0046224\times10^{5}$,					
$C_{71}=8.7560889\times10^{6}$,	$C_{73}=-1.1770643\times10^{6}$,					
$C_{80}=-2.2555292\times10^{8}$,	$C_{82}=-4.7697720\times10^{8}$,	$C_{84}=-2.2736149\times10^{7}$,				
$C_{91}=-8.4104501\times10^{8}$,	$C_{93}=-8.5592789\times10^{8}$,	$C_{95}=-1.0439150\times10^{8}$.				

2.3 Features of the surface

A contour plot of the potential energy surface is shown in Fig. 1. It is seen that there is a single global minimum in the geometry. The global minimum energy is -34.43607 cm^{-1} at $R_e=6.95a_0$ and $\theta_e=72.5°$. The linear Ne-Be-H geometry (-11.34 cm^{-1} at $R_e=9.10a_0$) is higher in energy (-25.96 cm^{-1} at R_e=8.45a_0) than the linear Ne-H-Be geometry. The potential is seen to be rather flat, making possible large amplitude motions.

3 Rovibrational energy levels calculation

3.1 Computational method

The detailed procedure for the calculation of eigenvalues and eigenfunctions was described in Ref. [22–24]. Here we only give the main points. The Hamiltonian with BeH frozen at its equilibrium distance can be expressed as

$$H=-\frac{\hbar}{2mR}\frac{\partial^2}{\partial R^2}R+\frac{\hbar^2}{2mR^2}(\hat{J}-\hat{j})^2+b_{\mathrm{BeH}}\hat{j}^2+V(R,\theta), \tag{8}$$

where $\hat{J}$ denotes the total angular momentum operator of the Ne-BeH complex, $\hat{j}$ means the angular momentum operator of rigid BeH molecule and b_{BeH} is rotational constant, m is the

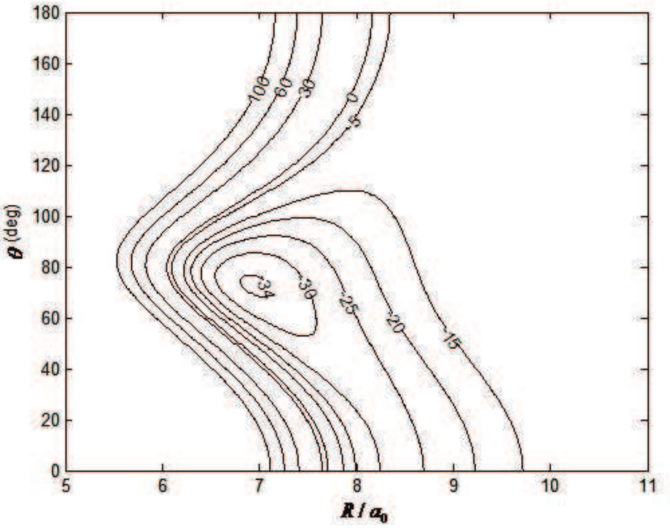

Figure 1: Contour plot of the potential energy surface for the Ne-BeH complex (in cm^{-1}).

reduced mass of the complex, and $V(R,\theta)$ is the Ne-BeH interaction potential. In the body-fixed coordinate system with the z-axis attached to R, the nuclear Schrödinger equation may be written as

$$H\psi_i^{JMp}(R,\theta,\varphi,\alpha,\beta)=E_i^{Jp}\psi_i^{JMp}(R,\theta,\varphi,\alpha,\beta). \tag{9}$$

The eigensolutions are labeled by good quantum numbers: J for the total angular momentum of the Ne-BeH complex, M for the magnetic quantum number and $p=\pm 1$ for the total parity of the wave function. The wavefunction depends on five variables: the intermolecular stretch coordinate R, the pair of angles (α,β) which are Euler angles for transforming between the space and body-fixed coordinate frames, and the pair of angles (θ,φ) which denote the orientation of the BeH bond axis relative to the body-fixed system. The index i stands for the different energy levels with a given set of J,M,p. The wave functions are expanded into a basis set

$$\psi_i^{JMp}(R,\theta,\varphi,\alpha,\beta)=\frac{1}{R}\left(\frac{2J+1}{4\pi}\right)^{1/2}\sum_{q=0}^{q_{\max}}\sum_{j=0}^{j_{\max}}\sum_{k=0\mathrm{or}1}^{\min(j,J)} c_{q,jk}^{Jpi}\chi_q(R)\Phi_{jk}^{JMp}(\theta,\varphi,\alpha,\beta), \tag{10}$$

where the angular basis functions are parity-adapted as

$$\Phi_{jk}^{JMp}(\theta,\varphi,\alpha,\beta)=N_k\Big(D_{MK}^{J*}(\alpha,\beta,0)Y_{jk}(\theta,\varphi)+p(-1)^J D_{M-K}^{J*}(\alpha,\beta,0)Y_{j-k}(\theta,\varphi)\Big). \tag{11}$$

Here, D_{MK}^{J*} is an element of a Wigner rotation matrix, Y_{jk} a spherical harmonic. The normalization factor N_k is $1/2$ for $k=0$ and $1/\sqrt{2}$ else. The sum over k starts from 1 when $p(-1)^J$ is -1, otherwise it begins with $k=0$.

The stretching basis function $\chi_q(R)$ has been determined as numerical eigensolutions of the vibrational Schródinger equation

$$\left(-\frac{\hbar^2}{2m}\frac{\partial^2}{\partial R^2}+V(R,72.5^\circ)\right)\chi_q(R)=E_q\chi_q(R), \tag{12}$$

where $V(R,72.5^\circ)$ is a cut of the Ne-BeH interaction potential at an angle of 72.5° which is the angle of minimum energy geometry. This choice has two advantages: simplifying the interpretation of the wave function and minimizing the required $q_{\max}$. When $\chi_q(R)$ has been obtained, the Hamiltonian matrix can be set up in terms of the basis functions, the rovibrational energies and the expanded coefficients $c_{q,jk}^{J,pi}$ are obtained from solution of the corresponding secular equation.

3.2 Theoretical results

A self-written Fortran code [25] is used to calculate the bound states energy levels of the Ne-BeH complex. After careful test we expand potential in Legendre polynomials up to $\lambda_{\max}=12$. The basis set parameter $j_{\max}$ and $q_{\max}$ is 35 and 30, respectively. The rotational constant b_{BeH} of BeH is 10.316417 cm^{-1} from the NIST Standard Reference Database [26]. The numerical integration over R is performed with 300 equidistant grids distributed from 5.0 to $16a_0$. The schemes of the energy levels of the Ne-BeH complex are presented in Fig. 2.

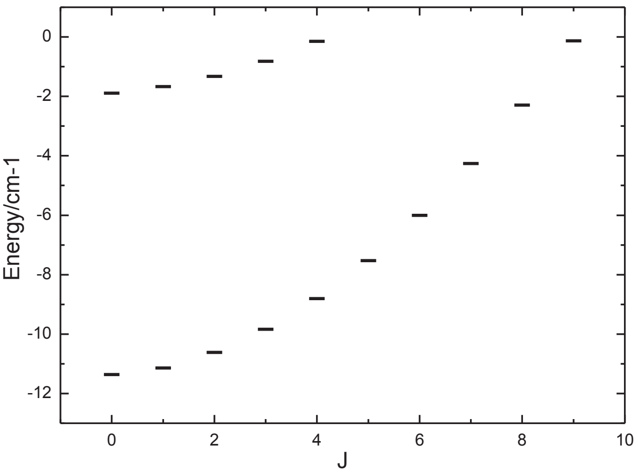

Figure 2: Schemes of the rovibrational energy levels with $J\leq 9$ of the Ne-BeH complex.

The column 5 in Table 2 shows the assignment of energy levels. The symbol n_{vdW} only represents the counter of the stretching/bending nodes. K is the projection of $\hat{J}$ onto the body-fixed intermolecular axis z under the Coriolis decoupling approximation, and its expectation value is calculated as

$$\langle K\rangle=\langle j_z J_z\rangle^{1/2}=\left(\sum_{q,j,k}K^2C^2_{qjk}\right)^{1/2}. \tag{13}$$

It can be seen the $\langle K\rangle$ value is close to the corresponding K in most situations, because of the neglectable off-diagonal Coriolis coupling terms whose order of magnitude is about 0.1 cm^{-1}. Thus, K can be considered as a good quantum number approximately. The inclusion of Coriolis interaction will further introduce asymmetry splitting of the levels with $K\geq 1$, which can be designated by e or f according to the value 1 or -1 of spectroscopic parity $p\times(-1)^J$. For $K=0$ only e levels exist. Table 2 shows that all the values of K with $J\leq 9$ is close to zero. It indicates that only e levels exist for the Ne-BeH complex.

Table 2: Calculated bound state levels(in cm^{-1})and corresponding assignments for J from 0 to 9 for $n_{vdW}=0$.

J	E	P	$\langle K\rangle$	$(n_{vdW},K,e/f)$
0	-11.3614	$+$	0.00	(0,0,e)
1	-11.1383	$-$	0.00	(0,0,e)
2	-10.6164	$+$	0.00	(0,0,e)
3	-9.8370	$-$	0.01	(0,0,e)
4	-8.8042	$+$	0.01	(0,0,e)
5	-7.5236	$-$	0.02	(0,0,e)
6	-6.0040	$+$	0.02	(0,0,e)
7	-4.2552	$-$	0.02	(0,0,e)
8	-2.2916	$+$	0.02	(0,0,e)
9	-0.1330	$-$	0.02	(0,0,e)

4 Conclusions

The first high quality *ab inito* potential energy surface for the Ne-BeH van der Waals complex has been developed by the CCSD(T) method and the avqz +33211 basis set. The supermolecule method is performed in a total of 228 configurations for the ab initio calculation. The counterpoise procedure of Boys and Bernardi is used to correct for basis set superposition error. The corrected *ab inito* single point interaction energies are fitted to an analytic potential model. It is found that there is a single global minimum located in the geometry. The global minimum energy is -34.43607 cm^{-1} at $R_e=6.95a_0$ and $\theta_e=725.5°$. Based on this potential, the rovibrational energy level structure of the Ne-BeH complex is calculated. It shows that all the values of K with $J\leq 9$ is close to zero. That indicates only e levels exist for the Ne-BeH complex. We expect the present results could be helpful for the experimental and theoretical investigation in the future.

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References

[1] Y. J. Xu and A. R. W. McKellar, Mol. Phys. 88 (1996) 859.
[2] G. C. Groenenboom and N. Balakrishnan, J. Chem. Phys. 118 (2003) 7380.
[3] A. I. Boothroyd, P. G. Martin, and M. R. Peterson, J. Chem. Phys. 119 (2003) 187.
[4] H. Cybulski, R. V. Krems, H. R. Sadeghpour, *et al.*, J. Chem. Phys. 122 (2005) 094307.
[5] G. C. Groenenboom and I. M. Struniewicz, J. Chem. Phys. 113 (2000) 9562.
[6] M. Tacconi, E. Bodo, and F. A. Gianturco, Theor. Chem. Acc. 117 (2007) 649.
[7] R. V. Krems, Int. Rev. Phys. Chem. 25 (2006) 283.
[8] H. L. Bethlem and G. Meijer, Int. Rev. Phys. Chem. 22 (2003) 73.
[9] J. Weinstein, R. deCarvalho, T. Guillet, B. Friedrich, and J. M. Doyle, Nature 395 (1998) 148.
[10] N. Balakrishnan, G. C. Groenenboom, R. V. Krems, and A. Dalgarno, J. Chem. Phys. 118 (2003) 7386.
[11] K. Raghavachari, G. W. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. 157, 479 (1989).
[12] C. Hampel, K. Peterson, and H.-J. Werner, Chem. Phys. Lett. 190 (1992) 1.
[13] M. J. O. Deegan and P. J. Knowles, Chem. Phys. Lett. 227 (1994)321.
[14] S. M. Cybulski and R. R. Toczylowski, J. Chem. Phys. 111 (1999) 10520.
[15] S. F. Boys and F. Bernardi, Mol. Phys. 19 (1970) 553.
[16] MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from R. D. Amos, A. Berning, D. L. Cooper, *et al.*
[17] R. Bukowski, J. Sadlej, B. Jeziorski, *et al.*, J. Chem. Phys. 110 (1999) 785.
[18] G. C. McBane and S. M. Cybulski, J. Chem. Phys. 110 (1999) 1734.
[19] Z. Q. Wang, M. Y. Gong, E. Y. Feng, and Z. F. Cui, Chem. Phys. Lett. 443 (2007) 237.
[20] K. T. Tang and J. P. Toennies, J. Chem. Phys. 80 (1984) 3726.
[21] Z. Q. Wang, M. Y. Gong, Y. Zhang, E. Y. Feng, and Z. F. Cui, J. Chem. Phys. 128 (2008) 044309.
[22] E. Y. Feng, W. Y. Huang, Z. F. Cui, and W. J. Zhang, J. Mol. Struct. (Theochem.) 724 (2005) 95.
[23] E. Y. Feng, Z. Q. Wang, M. Y. Gong, and Z. F. Cui, J. Chem. Phys. 127 (2007) 174301.
[24] Z. Q. Wang, M. Y. Gong, Y. Zhang, E. Y. Feng, and Z. F. Cui, J. Chem. Phys. 128 (2008) 044309.
[25] E. Y. Feng, W. Y. Huang, Z. F. Cui, and W. J. Zhang, J. Mol. Struct.(Theochem.) 724 (2005) 195.
[26] Standard Reference Database. Available from `http://webbook.nist.gov/chemistry/`