

Intermolecular vibrations in the benzene-neon complex based on *ab initio* and SAPT potentials



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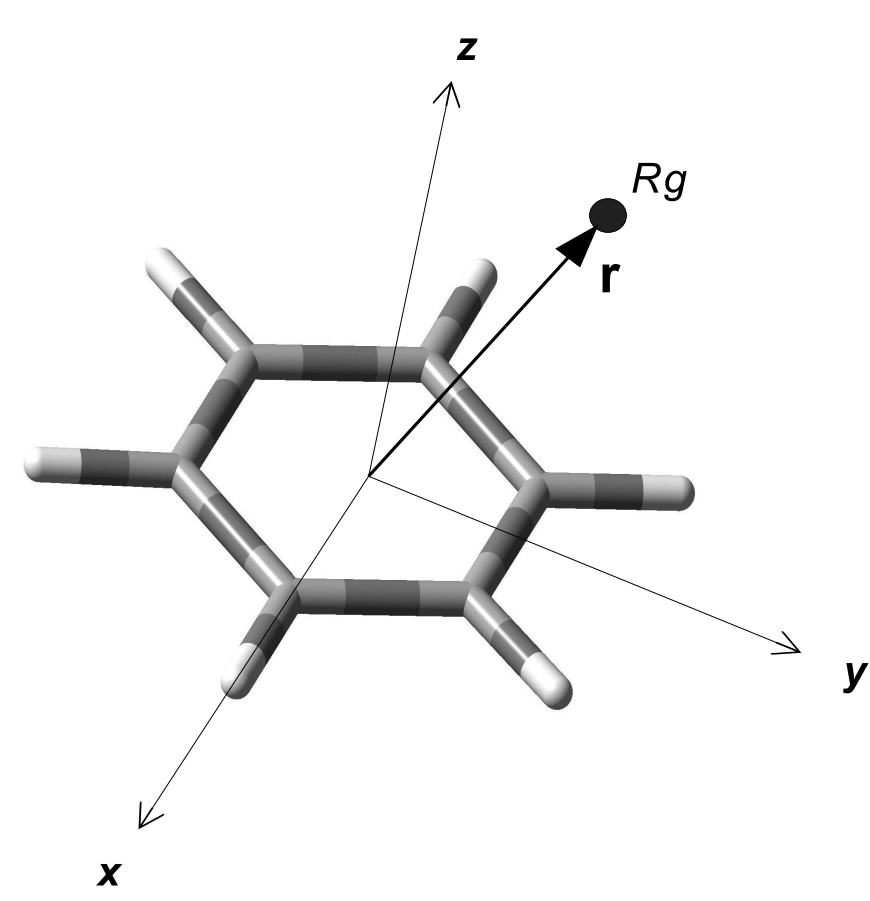
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1. Motivation

The complexes of aromatic molecules with rare gas atoms have been the subject of intensive research in the last few decades. Such interest is motivated by the fact that these complexes are exemplary models to study many phenomena at the microscopic level, for example, solvation and physisorption on surfaces, intramolecular vibrational redistribution and vibrational predissociation. The complexation of these complexes is mostly due to the domination of the dispersion component of the interaction energy and these complexes are considered as prototypical with dominating dispersion. Most of the experimental and theoretical studies focus on the complexes of aromatic molecules with Ar. However, the experimental data available for complexes with the lighter Ne atom are relatively scarce. Recently, there has been some increase of the interest in the experimental study of the complexes with Ne by supersonic cooling, stimulated-emission pumping resonant two-photon ionization and Fourier transform microwave spectroscopy [1-3]. Assignment of the vibrational energy patterns can be problematic for such complexes, because of the large amplitude intermolecular motion of Ne. Therefore, theoretical calculations are needed to confirm the available experimental data.

2. Electronic structure calculations



The position of the Rg atom (Ne) with respect to the benzene monomer can be described by vector \mathbf{r} in Cartesian (x, y, z) or spherical coordinates (r, θ, ϕ) .

Two alternative methods were used to calculate the interaction energy of the complex E_{int} - *ab initio* supermolecular and symmetry-adapted perturbation theory (SAPT).

1. In supermolecular method $E_{\text{int}} = E_{\text{AB}} - E_{\text{A}} - E_{\text{B}}$, where E_{AB} , E_{A} and E_{B} are the energies of the whole complex AB (dimer) and of separate molecules A and B (monomers). The *gold standard* CCSD(T) method (coupled cluster level including single and double excitations supplemented by triple excitation) is a good choice for this complex.

2. E_{int} decomposed into energy components within the SAPT theory is written as follows [5],

$$E_{\text{int}}^{\text{SAPT}} = E_{\text{elst}}^{(1)} + E_{\text{exch}}^{(1)} + E_{\text{ind}}^{(2)} + E_{\text{exch-ind}}^{(2)} + E_{\text{disp}}^{(2)} + E_{\text{exch-disp}}^{(2)} + \Delta^{3-\infty},$$

where $E_{\text{elst}}^{(1)}$ is the first-order electrostatic energy, $E_{\text{exch}}^{(1)}$ is the first-order exchange energy, $E_{\text{ind}}^{(2)}$ and $E_{\text{disp}}^{(2)}$ are the second-order induction and dispersion energies, respectively, and $E_{\text{exch-ind}}^{(2)}$ and $E_{\text{exch-disp}}^{(2)}$ are their exchange counterparts.

4. Van der Waals vibrational states

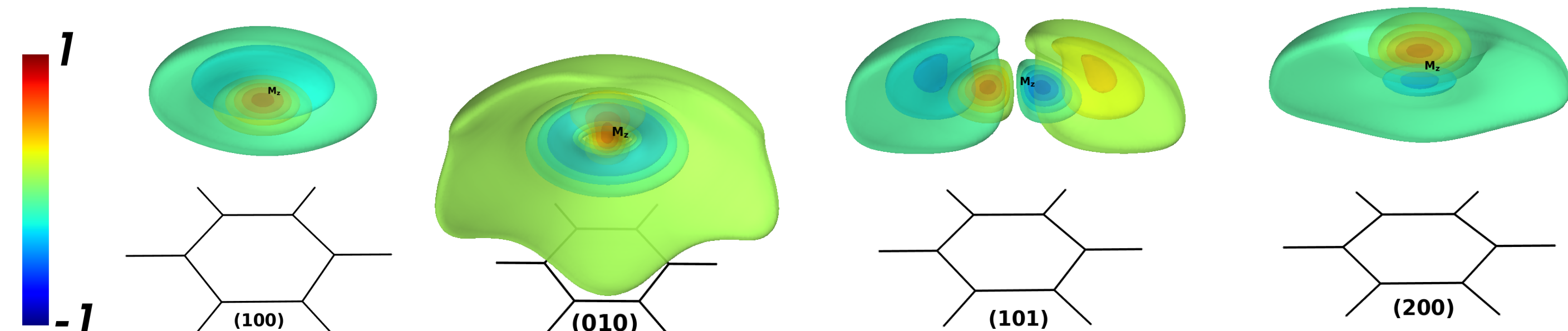
Vibrational 3D Schrödinger equation

$$[T_t^{\text{V}}(\mathbf{r}) + V(\mathbf{r}) - E_N^{\text{V}}]\Psi_N^{\text{V}}(\mathbf{r}) = 0,$$

where $T_t^{\text{V}}(\mathbf{r})$ is the kinetic energy term. The equation is solved using the implemented variational method [6,7] with harmonic oscillator functions centered at the global minimum \mathbf{M}_z to obtain energy levels and wave functions (WF) of vdW vibrational modes. The quantum numbers N chosen as (n_s, n_b, l) of harmonic oscillator were used for the assignment of the vibrational energies and the irreducible representations of point group C_{6v} was used for labeling the lowest states.

Comparison of the theoretical and empirical [4] vibrational energy levels. The energies are given relative to the ground state energy E_{000} in cm^{-1} .

n	Γ_{6v}	$n_s n_b l$	Empir.	CCSD(T)	SAPT
0	A_1	000	42.5	43.1	44.1
1	E_1	001	20.1	20.3	21.1
2	A_1	100	25.8	26.1	25.9
3	E_2	002	36.8	36.5	37.6
4	E_1	101	40.2	39.2	39.7
5	A_1	200	40.5	39.3	39.7
6	A_1	010	47.2	45.9	46.2



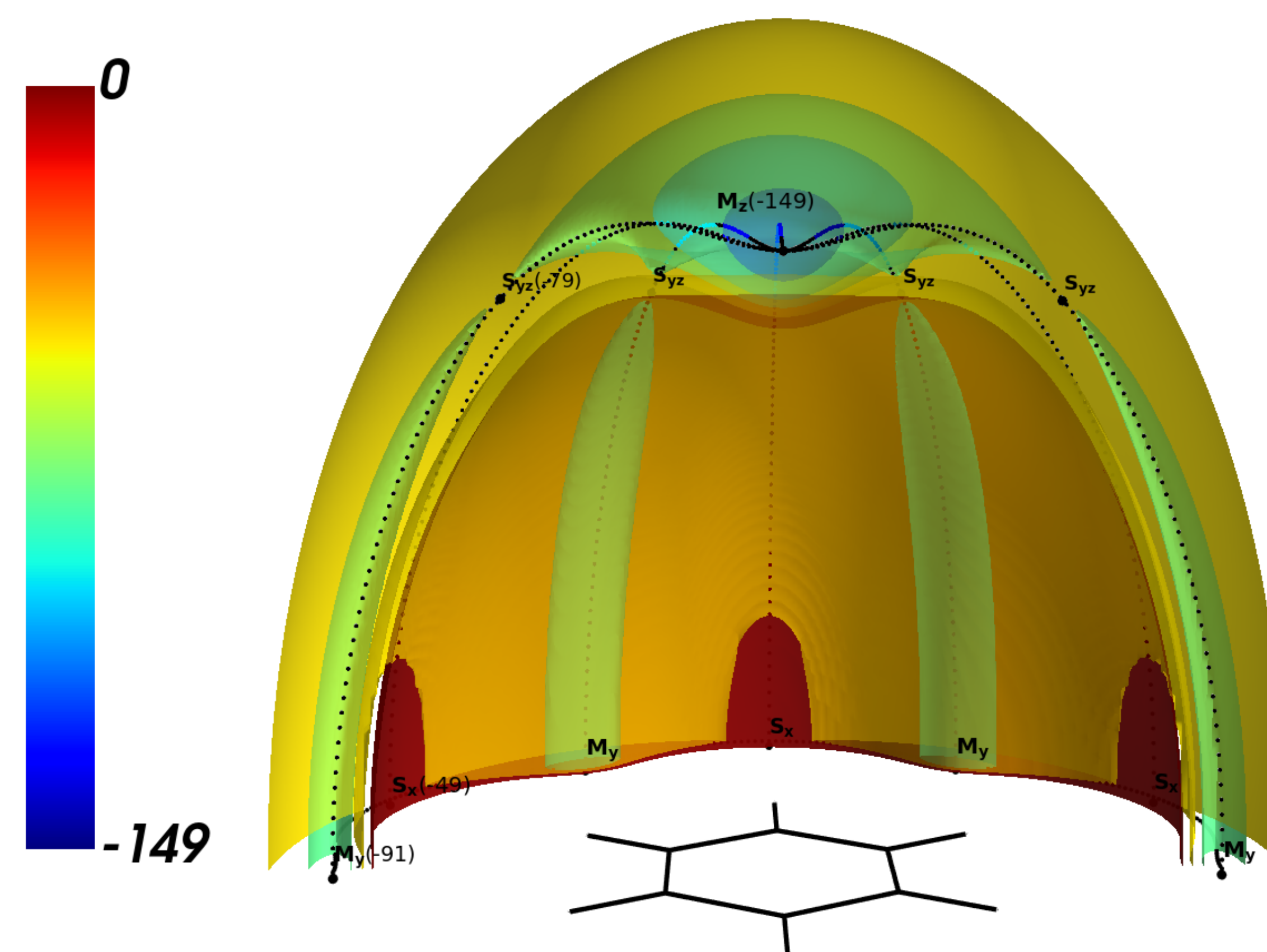
3D isopotential surfaces of the normalized WFs of the lowest vibrational states for the CCSD(T) potential. The WF isovalues differ by 0.2, where the maximum value of 1.0 corresponds to the WF maximum.

3. Potential Energy Surface (PES)

The calculated single-point E_{int} CCSD(T) and SAPT energies have been used to build an analytical potential which general form can be written as follows

$$V(\mathbf{r}) = f_{\text{sh}}(r)V_{\text{sh}}(\mathbf{r}) + f_{\text{ln}}(r)V_{\text{ln}}(\mathbf{r}).$$

The short-range $V_{\text{sh}}(\mathbf{r})$ and the long-range $V_{\text{ln}}(\mathbf{r})$ parts are found separately and damped by the appropriate functions $f_{\text{sh}}(r)$ and $f_{\text{ln}}(r)$ [5-7]. The parameters of $V_{\text{sh}}(\mathbf{r})$ were found with a non-linear optimization algorithm, and expansion coefficients $V_{\text{ln}}(\mathbf{r})$ were found using monomer properties (multipole moments and dynamic polarizabilities) [9,10].



3D The cut of the isopotential surfaces for $x > 0, z > 0$. \mathbf{M}_z and \mathbf{M}_y stand for the global and local minimum, respectively, while \mathbf{S}_{yz} and \mathbf{S}_x are the saddle points. The energy values are in cm^{-1} . The scale of the space coordinates is $x : y : z = 2 : 2 : 1$.

5. Conclusions and prospects

1. The prototypical complex with light Ne atom has been studied theoretically at such advanced level of theory for the first time.
2. The proposed methodology can be applied for the complexes of other aromatic molecules with Ne.
3. Similar methodology can be applied for the complexes of aromatic molecules with alkali-metal and alkaline-earth-metal atoms. This study motivated by recent experimental interest in cooling the polyatomic molecules [8]. Some work has been already done in this direction [9,10].

6. References

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