

Potential energy surface and intermolecular dynamics of pyridine-lithium complex



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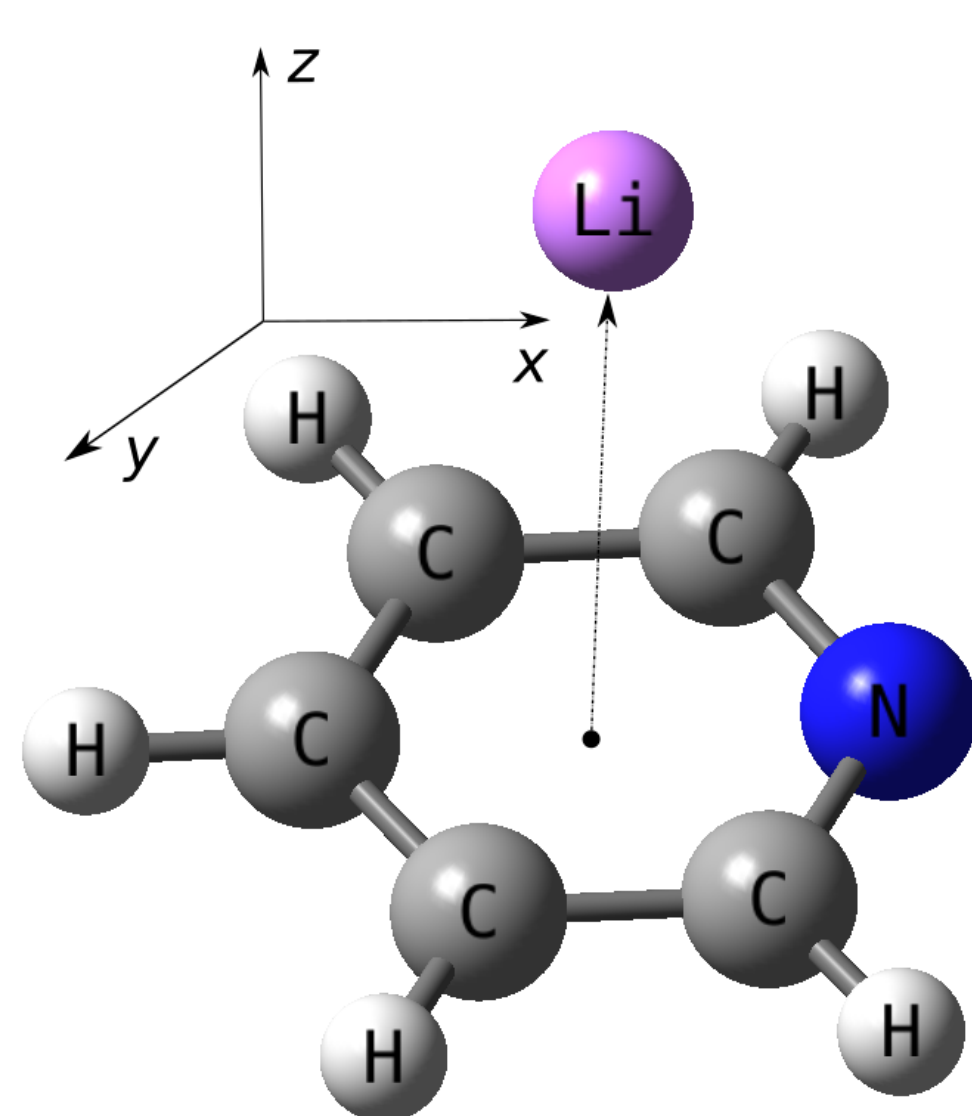
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1. Motivation

Recently there has been an increasing experimental interest to cool the polyatomic molecules [1]. Presence of rotation and vibrations compared to atoms allows for many applications such as quantum computing and simulation [2], and high precision measurements [3]. On the other hand, the additional degrees of freedom bring up new challenges both for experiment and theory. The density of vibrational energy levels imposes desirable requirements on the diagonality of Franck-Condon factors, and at the same time complicates its cooling due to energy loss resulting from inelastic collisions. Pyridine molecule is a prospective candidate used as a partner for Li due to its large dipole moment - 2D.

Another reason comes from the need of interpretation of the molecular spectra. The complexes of pyridine with Li, Ca and Sc have been already studied by means of laser spectroscopy [4]. The authors used zero-electron-kinetic-energy spectroscopy to determine the binding and ionization energies as well as intermolecular vibrational energies. However, the accurate assignment of the energies requires an accurate potential that will be used for the solution of 3D Schrödinger equation [5].

2. Electronic structure methods

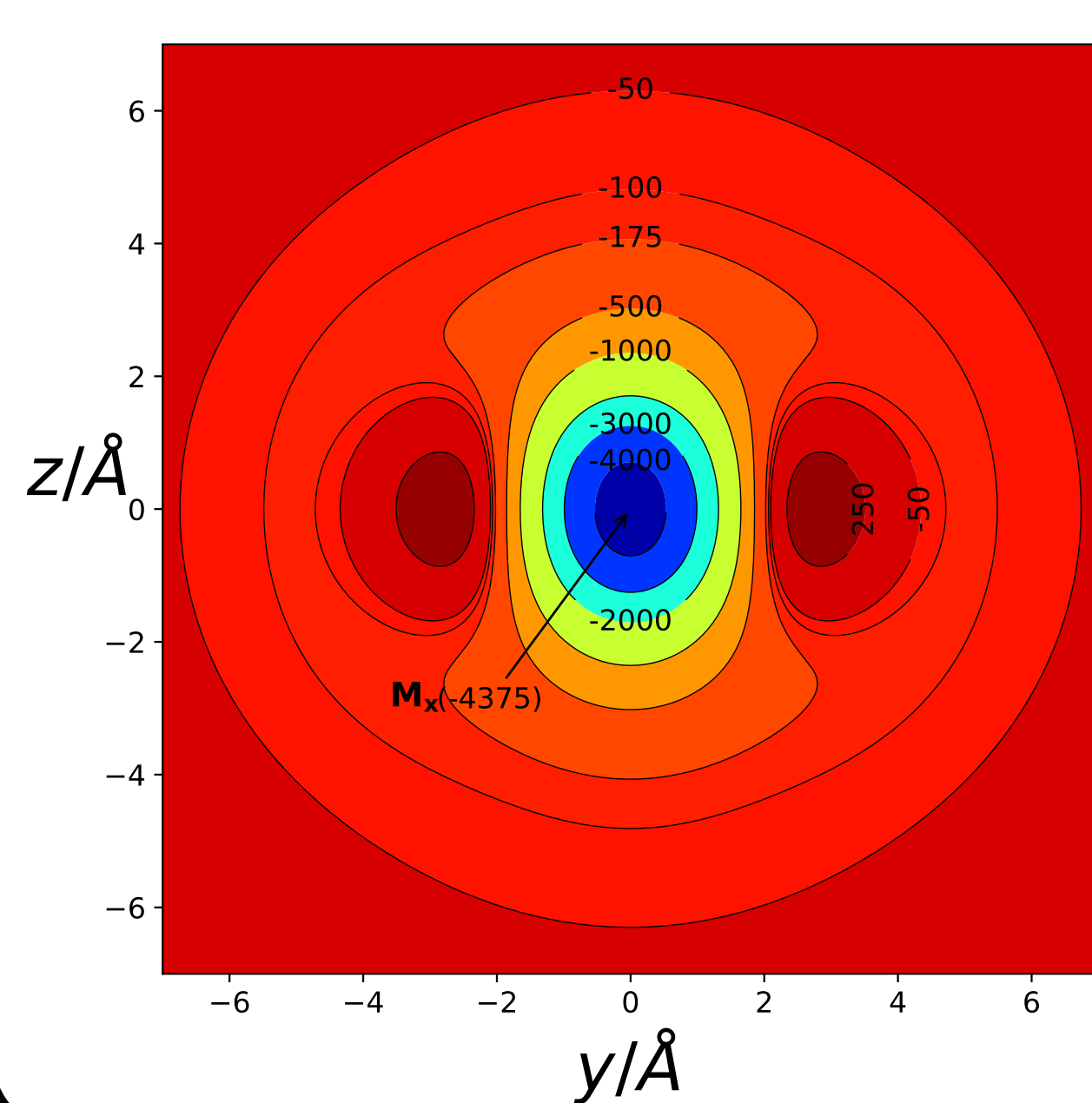


The interaction energy of the complex E_{int} is obtained with the supermolecular *ab initio* method, and the basis set superposition error is removed by using the counterpoise correction. A discrete set of different arrangements of Li and pyridine with respect to each other. The Li position vector \mathbf{r} is described with respect to the molecular system of axes shown in Figure. Rigid monomer approximation is used in this study.

PESs are evaluated using the following steps.

- 1 An excessive number, ~ 3000 , of Li positions are first calculated using second-order Møller-Plesset perturbation theory with spin-restricted open-shell RHF reference - RMP2 with aug-cc-pVTZ(H)/aug-cc-pCVTZ(C,Li) one electron basis sets with all orbitals correlated.
- 2 A smaller number of Li positions, ~ 500 , are calculated using more expensive RCCSD(T) with aug-cc-pVTZ(H)/aug-cc-pVTZ(C,Li) basis sets supplemented by $3s3p2d1f1g$ midbond functions located at the point $\mathbf{r}/2$ with frozen core approximation (RCC1).
- 3 Another more computationally expensive method is used for ~ 200 of Li positions, RCCSD(T) with aug-cc-pVTZ(H)/aug-cc-pCVTZ(C,Li) basis sets supplemented by $3s3p2d1f1g$ midbond functions located at the point $\mathbf{r}/2$ with all orbitals correlated (RCC2).

4. Complex topology



The complex is characterized by one global minimum \mathbf{M}_x located in the monomer plane opposite to N atom and two shallow local minima above the plane. There are no bound states in the local minima and there is no tunneling motion of Li between them. The Figure represents the cut of the potential at $x = x_e$ in yz -plane.

3. Analytical PES with long-range part

The following form of the analytical PES is used. The short-range part is taken using many-body expansion form [5]

$$V_{\text{short}} = V_0 + W_0 \left[\sum_k V_2(r_k) + \sum_{l < k} V_3(r_k, r_l) + \sum_{m < l < k} V_4(r_k, r_l, r_m) \right],$$

where r_k is the distance between the Li atom and the k^{th} atom of pyridine. The long-range part is given by the following expression [6]

$$V_{\text{long}} = - \sum_{i=6}^8 \sum_{0 < m \leq l} \frac{C_i^{l,m}}{R^i} \Omega_{lm}(\theta, \phi),$$

where $\Omega_{lm}(\theta, \phi)$ is the tesseral harmonics basis. The coefficients $C_i^{l,m}$ mostly describe the dispersion interaction in the long-range.

The construction of an analytical PES includes the following steps.

1. The long-range part of the potential V_{long} is calculated using the first principles [6].
2. With the long-range part fixed, the potential $V = V_{\text{short}} f_{\text{short}} + V_{\text{long}} f_{\text{long}}$ with damping functions f_{short} and f_{long} , valid in the whole physically meaningful interaction, is constructed using E_{int} found with RMP2.
3. The procedure 1-2 is repeated using more computationally expensive RCC1 and RCC2 methods, starting with RMP2 parameters as the initial values in the nonlinear Levenberg-Marquardt optimization algorithm. The total number of the potential parameters ~ 70 .

5. Intermolecular vibrational energies

3D Schrödinger equation is solved using the implemented variational method [5,7] with harmonic oscillator functions centered at the global minimum \mathbf{M}_x to obtain energy levels and wave functions of vdW vibrational modes. The nodal pattern of the wave functions was used for the assignment.

The table contains binding D_e , dissociation D_0 , and vibrational energies in cm^{-1}

		RMP2	RCC1	RCC2	Exp. [4]
	D_e	4375	4588	4752	-
	D_0	3897	3993	4110	4099
State	$n_x n_y n_z$				
1	001	76	85	86	84
2	010	96	106	103	102
3	100	432	456	460	446
4	011	168	182	184	-

6. Conclusions and Prospects

1. Highly-accurate analytical PES has been constructed for pyridine-Li complex with rigid-monomer approximation.
2. Topological and the structural parameters of the complex have been studied.
3. Intermolecular vibrational energies have been calculated and preliminary assignment of the lowest states is made.
4. Elastic and inelastic cross sections will be evaluated using the constructed analytical PES.
5. Non-rigidity of the pyridine monomer has to be taken into account due to the coupling of the intermolecular modes with intramolecular ones.

7. References

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