Dynamics of aromatic molecules with alkali and alkaline-earth metal atoms with application to sympathetic cooling

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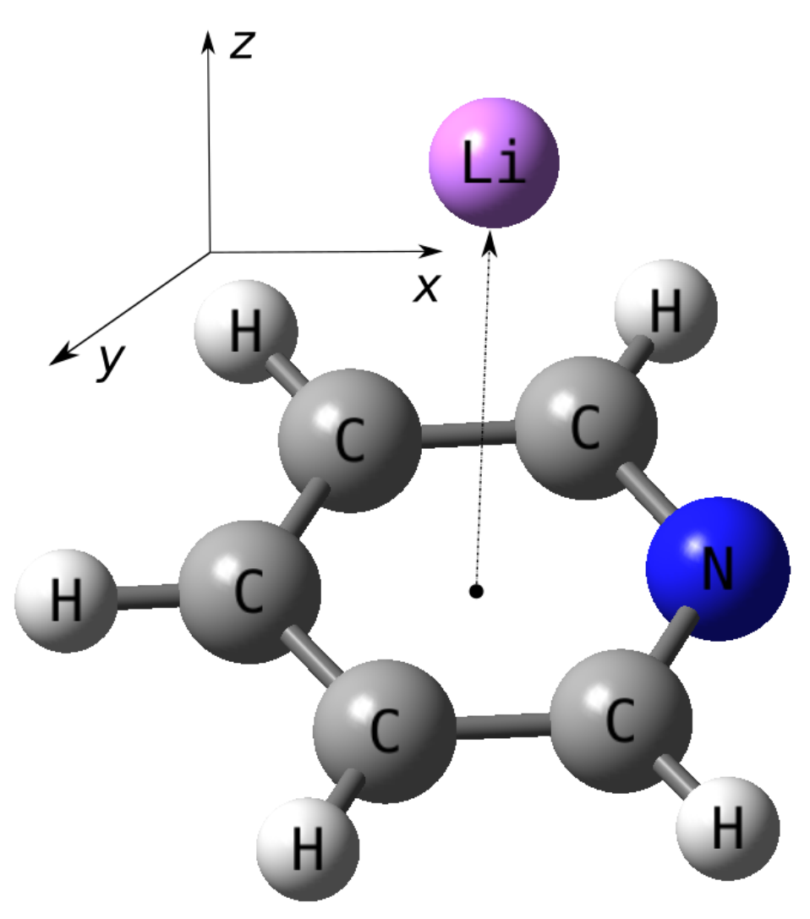
1. Motivation

To generate molecules at temperatures below the millikelvin range, an additional cooling process is necessary. Sympathetic cooling, a method that cools precooled molecules by exposing them to ultracold atomic gas, is a promising approach. The capacity to laser-cool polyatomic molecules, including symmetric-top molecules, is crucial for future advancements in these fields [1]. The studies where these atoms interact with polyatomic molecules are limited, both theoretically and experimentally. Cold collisions and sympathetic cooling of aromatic molecules, such as benzene, have been previously investigated theoretically, but only in conjunction with He and other rare gas atoms [2].There remains a deficiency in our understanding of how large polyatomic molecules interact with alkali and alkaline-earth metal atoms at low temperatures. This uncertainty extends to the effectiveness of sympathetic cooling for these molecules at lower temperatures. In addition to the potential for sympathetic cooling of aromatic molecules, there is interest in these complexes for other reasons. The complexes of pyridine with Li, Ca, and Sc have been studied using laser spectroscopy [3], and theoretical data is necessary for spectral assignment. Our objective is to theoretically examine the spectroscopic and collisional behavior of polyatomic aromatic molecules (benzene, pyridine, furan, and pyrrole) immersed in ultracold atomic gases. The initial steps toward evaluating Potential Energy Surfaces (PES) for the complexes have already been taken [4, 5].

2. Electronic structure methods



The interaction energy of the complexes 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 arrangement of metal and aromatic molecule with respect to each other was used. The position vector $\mathbf{r}$ of the metal atoms is described with respect to the molecular system of axes shown in Figure. Rigid monomer approximation is used in this study.

We used augmented correlation-consistent polarized core-valence quadruple-ζ quality basis sets (aug-cc-pCVQZ) for Li, Na, and Mg, and aug-cc-pVTZ for H and C. For K, Rb, Cs, Ca, Sr, and Ba atoms, scalar relativistic effects are accounted for by utilizing small-core relativistic energy-consistent pseudopotentials (ECPs) to substitute the inner-shell electrons. The basis sets are supplemented by $3s3p2d1f1g$ midbond functions located at the point $\mathbf{r}/2$. We utilize the coupled cluster approach in a closed-shell (or spin-restricted open-shell) configuration. This method involves single, double, and noniterative triple excitations [CCSD(T)], and the calculations are initiated from the starting point of the HF orbital, which is either restricted and closed-shell or open-shell.

4. Intermolecular rovibrational energies

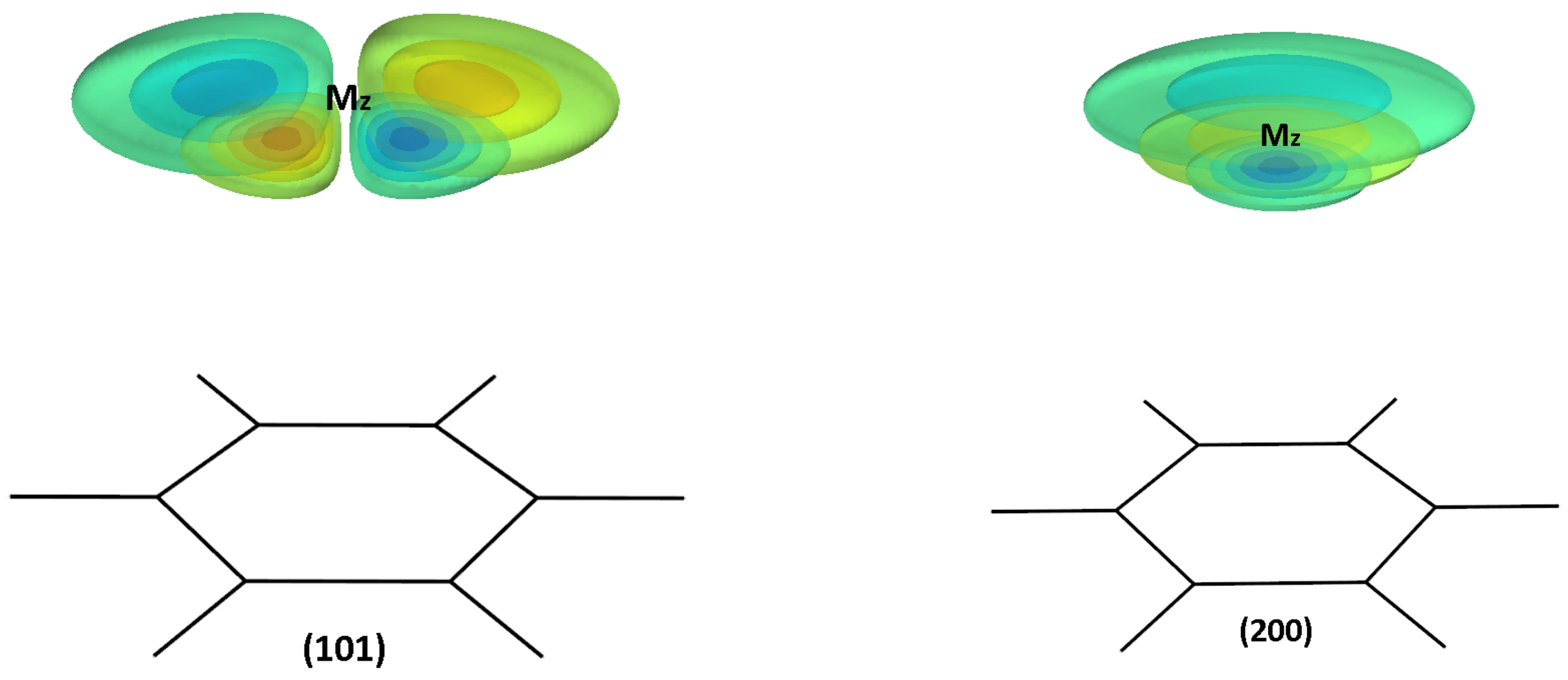
The benzene-metal complexes are characterized by two symmetrically-equivalent global minima $\mathbf{M_z}$ located above the monomer and six local shallow minima in the monomer plane with no tunneling between the global minima. The complexes with monomers of $C_{2\text{v}}$ are characterized by one global minimum $\mathbf{M_x}$ located in the monomer plane.

Binding D_e, dissociation D_0, and vibrational energies (cm^{-1}) for selected benzene-metal complexes

		Li	Na	Rb	Mg	Ca	Sr
	D_e	1580	790	1170	810	970	1150
	D_0	1350	650	1010	590	620	945
State	$n_s n_b l$						
1	001	120	75	84	69	91	95
2	100	142	90	110	112	123	117
3	002	210	141	155	130	173	184
4	101	245	156	183	166	189	173

3D nuclear Schrödinger equation is solved using the implemented variational method [6] with harmonic oscillator (HO) functions centered at the global minimum $\mathbf{M_z}$ (or $\mathbf{M_x}$) to obtain energy levels and wave functions of vdW vibrational modes. The nodal pattern of the wave functions (WF) was used for the assignment using HO quantum numbers (n_s, n_b, l) for benzene and (n_x, n_y, n_z) for the $C_{2\text{v}}$ monomers.

Normalized vibrational WFs of benzene-Li for (101) and (200) states



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 [6]

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

where r_k is the distance between the metal atom and the k^{th} atom of pyridine. The long-range part is given by the following expression [5,7]

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

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 parameters of the potential are found using the nonlinear Levenberg-Marquardt optimization algorithm. The total number of the potential parameters ∼50 for the complexes with monomers of $C_{2\text{v}}$ symmetry and ∼30 for benzene ($D_{6\text{h}}$). The coefficients reproduce *ab initio* E_{int} with root mean square error (RMSE) of an order of 0.5 cm^{-1} in the van der Waals region.

5. Collisional crossections

The code [6] was expanded to treat both elastic and inelastic collision problems. The outcomes were cross-verified using the MOLSCAT package [8]. While the *p*-wave significantly influences higher energy levels, the *s*-wave prevails in determining the cross section at lower energy levels. The first threshold energies, scattering lengths (a_{S}) and effective ranges (r_{eff}) were calculated.

Contr. of the *s*- and *p*- waves to the total cross sections at selected incident energies (benzene-metal)

	Li		Na	Rb	Mg	Ca	Sr
$E(\text{cm}^{-1})$	0.01	0.001	0.01	0.01	0.01	0.01	0.01
$\sigma(s)(\text{Å}^2)$	4500	37000	2600	1350	730	1250	800
$\sigma(p)$ (Å^2)	470	40	130	430	250	740	50

6. Conclusions and Prospects

1. The assignment of vibrational spectra is possible in terms of harmonic oscillator (HO) quantum numbers for the lowest energy states.
2. A correction to the vibrational spectra assignment for pyridine-Li and pyridine-Ca, as reported in [3], has been suggested.
3. The non-rigidity of the polar monomers needs to be considered due to the coupling between intermolecular modes and intramolecular ones to achieve higher accuracy.
4. A more comprehensive study of the collision problem, aimed at investigating resonances, will be conducted in the future.
5. The results obtained are currently being prepared for publication.

7. References

1. D. Mitra, N. B. Vilas, C. Hallas, L. Anderegg, B. L. Augenbraun, L. Baum, C. Miller, S. Raval, and J. M. Doyle, Science 369, 1366 (2020)
2. P. Barletta, J. Tennyson, and P. F. Barker, New J. Phys. 11, 055029 (2009)
3. S. A. Krasnokutski and D.-S. Yang, J. Chem. Phys. 130, 134313 (2009)
4. P. Wójcik, T. Korona, and M. Tomza, J. Chem. Phys. 150, 234106 (2019)
5. L. Shirkov and M. Tomza, J. Chem. Phys. 158, 094109 (2023)
6. L. Shirkov, V. Sladek, and J. Makarewicz, J. Chem. Phys. 152, 114116 (2020)
7. W. Rijks, M. van Heeringen, and P. E. S. Wormer, J. Chem. Phys. 90, 6501 (1989)
8. J. M. Hutson, C. R. Le Sueur, MOLSCAT, Comput. Phys. Commun. 241 (2019)