

Ab Initio Calculations for Inner-Shell Ionized and Excited States of Molecular Pyridine Clusters

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Abstract. *Ab initio* calculations are applied to the inner-shell ionizations and excitations of molecular pyridine clusters. We found theoretically that the C 1s $\rightarrow \pi^*$ transition is red shift while the N 1s $\rightarrow \pi^*$ transition is blue shifted. The red shift and blue shift increase with increasing cluster size. The ground state geometries of pyridine dimers and trimers are electrostatically stabilized with the molecular dipole anti-parallel to each other. The physical origin of the blue shifts in the N 1s regime is essentially ascribed to electrostatic interactions.

Keywords: *ab initio* calculations, core-to-valence excited state, pyridine clusters

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INTRODUCTION

Photoionization of clusters containing aromatic molecules has been investigated earlier in the regime of the first ionization energy, where characteristic red shifts of the appearance energies of clusters were observed in comparison with the ionization energy of the isolated molecule [1]. These red shifts are rationalized with the polarization (PL) effect by molecules surrounding a positively charged core-ionized molecule. On the other hand, photoexcitation of clusters containing aromatic molecules does not show such a red shift and a PL effect, because the core excited states are kept neutral. Recently, we have investigated the C 1s $\rightarrow \pi^*$ excitation in variable size benzene clusters [2], whose excited states undergo substantial red shifts up to 60 meV relative to the isolated molecule. This red shift is due to the PL effect induced by a localized core hole and is supported by an *ab initio* quantum chemical calculation using the GSCF3 code [3-5].

In the present work, GSCF3 is used to calculate core ionizations and core-to-valence excitations in the N 1s and C 1s regimes of pyridine clusters in comparison with the results of benzene clusters [2].

THEORETICAL METHODS

The GSCF3 program package [3-5] is designed specifically for molecular inner shell excitation and ionization. The GSCF3 approach is based on the Hartree-Fock self-consistent field (HF-SCF) to solve the energies and molecular orbitals of the system under investigation and the configuration interaction (CI) for correlated systems [5]. GSCF3 directly solves core-hole states as stationary points to keep from

variational collapse to the lowest state within one-Hamiltonian scheme [3]. The basis sets of Huzinaga et al. [6] are incorporated to afford any contraction scheme in addition to standard basis sets such as STO-3G and 4-31G. The initial guess for SCF orbitals is automatically produced from approximate density matrix over basis functions. The improved virtual orbital (IVO) [7], or static exchange (STEX), method explicitly taking into account the core hole in the fully-relaxed Hartree-Fock approximation for the core-hole state [8] is used to perform quantum calculations on core-excited molecules [3], where the virtual orbitals provide a good approximation to the term values of the core-to-Rydberg excitation features [8]. The core-to-valence excited states are obtained sequentially by the partial SCF method [3] with explicit consideration of the core hole [4], where the full-relaxed HF orbitals (STEX/IVO) are used as an initial guess for the core-to-valence excitation.

Primitive basis functions were taken from (73/7) and (63/5) contracted Gaussian-type functions of Huzinaga et al. [6]. They were augmented with polarization functions $\zeta_d = 0.617$ for C and N atoms. The contraction scheme was an extended basis set (3111121/31111/1) for the ionized C and N, a split-valence basis set of double ζ quality (621/41/1) for the unionized N and C atoms and (32) for H atoms. Diffuse functions were not included because Rydberg states are not the focus of this work. The present core-to-valence calculations ignore the zero point vibration energy and the electron correlation involving van der Waals interactions, which are expected to be more or less cancelled between the ground state and the core-excited state. A separate calculation is performed for each distinct chemical site in each configuration.

TABLE 1. Vertical ionization and $1s \rightarrow \pi^*$ excitation energies (in eV), oscillator strengths, and energy shifts (in eV) for the pyridine dimer. The site numbers for nitrogen and carbon atoms are shown in Fig.1a.

	Excitation Energy (eV)		Ionization Energy (eV)		Oscillator Strength	
	Monomer	Dimer (Shift)	Monomer	Dimer (Shift)	Monomer	Dimer
N01	399.245	399.289 (0.044)	404.397	404.255 (-0.142)	0.0106	0.0109
C02	286.722	286.715 (-0.007)	291.585	291.391 (-0.194)	0.0195	0.0191
C03	286.153	286.120 (-0.033)	290.653	290.476 (-0.176)	0.0119	0.0122
C04	286.082	286.029 (-0.053)	291.191	290.960 (-0.231)	0.0168	0.0180

TABLE 2. Vertical ionization and $1s \rightarrow \pi^*$ excitation energies (in eV), oscillator strengths, and energy shifts (in eV) for the pyridine trimer. The site numbers for nitrogen and carbon atoms are shown in Fig.1b.

	Excitation Energy (eV)		Ionization Energy (eV)		Oscillator Strength	
	Monomer	Dimer (Shift)	Monomer	Dimer (Shift)	Monomer	Dimer
N01	399.245	399.288 (0.043)	404.397	404.191 (-0.206)	0.0106	0.01117
C02	286.722	286.718 (-0.004)	291.585	291.328 (-0.257)	0.0195	0.01971
C03	286.153	286.123 (-0.030)	290.653	290.419 (-0.234)	0.0119	0.01219
C04	286.082	286.035 (-0.047)	291.191	290.900 (-0.291)	0.0168	0.01881
N12	399.245	399.336 (0.091)	404.397	404.134 (-0.263)	0.0106	0.01116
C13	286.722	286.705 (-0.017)	291.585	291.212 (-0.373)	0.0195	0.01901
C14	286.153	286.081 (-0.072)	290.653	290.318 (-0.335)	0.0119	0.01233
C15	286.082	285.977 (-0.105)	291.191	290.744 (-0.447)	0.0168	0.01910

Full geometry optimization for the pyridine dimer and trimer at the MP2 6-311G** level have been performed with the Gaussian suite of programs [9]. The calculations of pyridine dimer show more possible orientations due to the lower symmetry C_{2v} . The bonding in pyridine dimer can arise from both electrostatic interactions, mainly because of dipole and quadrupole moments, and from dispersion energy. A wide range of different intermolecular orientations provides an explanation for the complicated X-ray structure and underlines the possibility for the different phases in the solid state [10].

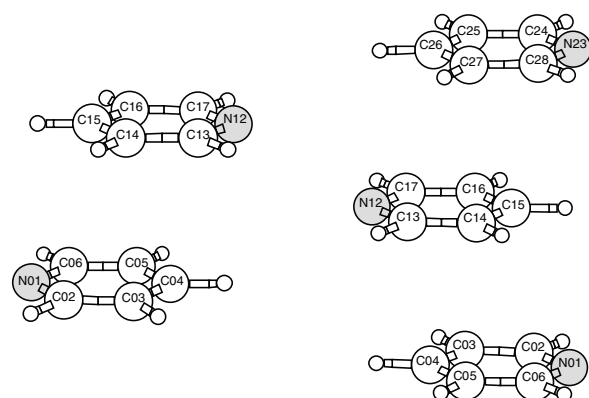
RESULTS AND DISCUSSION

The most stable pyridine dimer structure is found to be the parallel displaced structure, where the N atoms are opposing each other. It can be seen that for the anti-parallel displaced geometry of the dimer the positively charged H atom of one ring lies on top of the negatively charged nitrogen atom of the other ring, thus explaining the origin of the most stable geometry of the dimer. The C–N distance is found to be 1.345 Å, C–C distance 1.395 Å, and C–H distance 1.087 Å. The center-of-mass distance between the two rings is 3.32 Å in the perpendicular direction and is displaced by 1.24 Å along the plane (see Fig. 1a).

In the anti-parallel displaced geometry of pyridine trimer (see Fig. 1b), the middle pyridine is displaced with respect to the top as well as the bottom pyridine rings (which are stacked in a parallel configuration) to

the same extent as was found in the minimum energy configuration for the dimer, such that it consists of two anti-parallel displaced pyridine geometries. In contrast to the parallel displaced stacking interaction in benzene dimer, the stacking interaction in pyridine dimer, and trimer is likely to be influenced by the permanent dipole moment of pyridine.

Tables 1 and 2 show vertical C $1s$ ionization and singlet C $1s \rightarrow \pi^*$ excitation energies and oscillator strengths in the anti-parallel displacement for the pyridine dimer and trimer, respectively. These are obtained by using the HF solutions for the $1s$ hole states. The transition of the molecule splits due to a chemical shift induced by nitrogen in the heterocyclic system. Ortho carbon sites (C02, C13) have higher energy excitation than the meta (C03, C14) and para (C04, C15) carbon sites. The oscillator strengths in the C $1s \rightarrow \pi^*$ transitions are also found to be different between ortho, meta and para sites. We observe that the core ionization and excitation decrease in the sequence ortho – para – meta and ortho – meta – para, respectively. This can be partly understood considering the electronegativity of the nitrogen atom. The C $1s \rightarrow \pi^*$ excited state of pyridine clusters undergoes a substantial red shift relative to the molecule. Clearly, the sites next to the nitrogen site (ortho-carbon) show a negligible red shift, whereas the meta-carbon and para-carbon sites show a substantial red shift. This red shift is comparable to the red shift in benzene clusters [2].



a) anti-parallel dimer

b) anti-parallel trimer

FIGURE 1. MP2/6-311G** optimized geometries in the parallel displaced structure for the pyridine dimer (a) and pyridine trimer (b).

On the other hand, the $N\ 1s \rightarrow \pi^*$ excitation in the pyridine dimer and trimer is predicted to be blue shifted, as shown in Tables 1 and 2. In the parallel displaced dimer structure the blue shift is 44 meV (see Fig. 1a). In the trimer as shown in Fig. 1b, the N on the middle ring has the largest blue shift of 91 meV, whereas the N on the outer rings leads to a smaller blue shift of 43 meV. The $N\ 1s$ ionization energy has been assigned experimentally to 404.8 eV [11] and the $N\ 1s \rightarrow \pi^*$ ($3b_1$) transition is observed at 398.8 eV [11]. The present core-to-valence calculations ignore the zero point vibration energy and the electron correlation involving van der Waals interactions, which are expected to be more or less cancelled between the ground state and the core-excited state. The physical origin of the blue shift in the $N\ 1s \rightarrow \pi^*$ is essentially ascribed to electrostatic interactions (ES) in the anti-parallel dimer (see Fig. 2). The ES effect was evaluated by substituting each atom in the unexcited pyridine molecule by a point charge. The point charges are chosen in such way to reproduce the charge of individual atoms. We have observed that the $N\ 1s$ ionization energy increases as a function of relative horizontal displacement, where the $N\ 1s \rightarrow \pi^*$ energy is oscillating. This oscillation may indicate covalent intermolecular interactions such as charge transfer, because the ES curves are not oscillating. The error in the ES effect in the $N\ 1s$ ionization energy is 130 meV and in the $N\ 1s$ excitation energy 70 meV.

In summary, we have performed *ab initio* calculations of core-ionization and core-to-valence excitation energies on pyridine dimers and trimers in the $C\ 1s$ and $N\ 1s$ regimes. The $C\ 1s \rightarrow \pi^*$ transitions, in pyridine dimers and trimers are red shift relative to the molecule. On the other hand, the $N\ 1s \rightarrow \pi^*$ transitions in pyridine dimers and trimers are

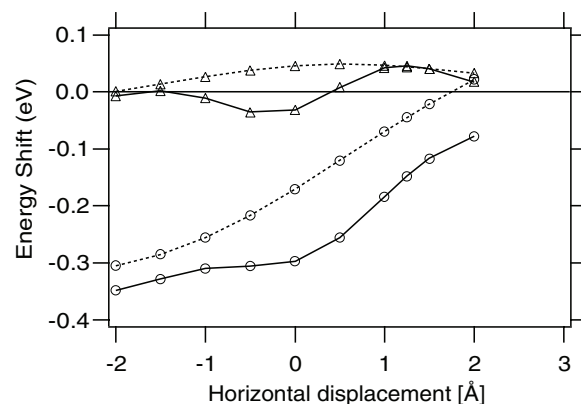


FIGURE 2. Calculated $N\ 1s \rightarrow \pi^*$ (triangles) and ionization (circles) energies in the anti-parallel pyridine dimer (full lines), depending on horizontal displacement relative to the equilibrium distance, where the negative displacement means approaching of the two nitrogen atoms. The dotted lines are calculated by approximating an unexcited pyridine molecule as point charges put on each atom.

calculated to be blue shifted relative to the molecule, which is rationalized in terms of electrostatic interactions between the molecules in clusters.

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REFERENCES

1. E. Rühl, P. Bisling, B. Brutschy, and H. Baumgärtel, *Chem. Phys. Lett.* **126**, 232 (1986).
2. I. L. Bradeanu, R. Flesch, N. Kosugi, A. Pavlychev, and E. Rühl, *Phys. Chem. Chem. Phys.* **8**, 1906 (2006).
3. N. Kosugi, and H. Kuroda, *Chem. Phys. Lett.* **74**, 490 (1980).
4. N. Kosugi, and H. Kuroda, *Chem. Phys. Lett.* **94**, 377 (1983).
5. N. Kosugi, *Theor. Chim. Acta* **72**, 149 (1987).
6. N. Huzinaga, J. Andzelm, M. Klobukowski, E. Eadzio-Andzelm, Y. Sakai, and H. Tatewaki, *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, 1984.
7. W. Hunt, W. Goddard, *Chem. Phys. Lett.* **3**, 414 (1969).
8. S. Iwata, N. Kosugi, and O. Nomura, *Jpn. J. Appl. Phys.* **17-S2**, 109 (1978).
9. M. Frisch, et al., *Gaussian 03, Revision C.02* (2004), Gaussian, Inc., Wallingford, CT.
10. D. Mootz, and H.-G. Wussow, *J. Chem. Phys.* **75**, 1517 (1981).
11. J. A. Horsley, J. Stöhr, A. P. Hitchcock, D. C. Newbury, A. L. Johnson, and F. Sette, *J. Chem. Phys.* **83**, 6099 (1985).