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Theoretical Study of Cadmium– and Mercury–Ammonia Exciplexes: Comparison with Experiment

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A quantum chemical calculation has been performed for complexes of a cadmium or mercury atom with ammonia by using relativistic effective core potentials (RECPs). It was shown that the luminescence from the exciplexes of the excited complexes was in good agreement with the experimental observations. The spin–orbit configuration interaction (SOCI) calculations showed that for Cd–NH_3, the energy difference between the $^3A_1$ and $^3A_2$ states was too small to determine the emission state. On the other hand, for Hg–NH_3, the energy difference was relatively large because of a relativistic effect. These results are consistent with the experimental observations.

Many studies of photosensitized reactions of the cadmium and mercury atoms have been carried out. Compounds such as amine or alcohol, which contain an N or an O atom, form exciplexes with excited triplet state cadmium and mercury.[1–16] Recently, we found an interesting result for photosensitized reactions of a cadmium atom with diamines, where two emission bands were observed in the blue and green regions.[6–9] From the temperature and pressure dependence of the emission intensities, it was suggested that these bands could be assigned to two kinds of 1 : 1 exciplexes between a cadmium atom and a diamine molecule. Furthermore, on the basis of kinetic and thermodynamic considerations, cyclic and acyclic exciplexes were assigned to the long- and short-wavelength bands, respectively. Several investigations for the Hg–NH_3 complex have been performed *via* another approach.[17–19]

For heavy-atom systems including cadmium and mercury, the interaction between the orbital and spin angular momenta of electrons in the molecule become important. The correlation diagram of the potential-energy curves for the dissociation with and without spin–orbit interactions for Cd–NH_3 or Hg–NH_3 is shown in Fig. 1. Past experiments have shown that for Hg–NH_3, $^3A_1$, which correlates Hg($^3P_1$) + NH_3, is distinguishable from $^3A_2$, which correlates Hg($^3P_0$) + NH_3, and it has been proposed that the emission state was the $^3A_2$ state.[14–17] For Cd–NH_3, on the other hand, there are no experimental data to distinguish between these two states except for the study by Umemoto *et al.*[3]

Theoretical studies for these systems have not been performed except for our previous *ab initio* calculations for Cd–ethylenediamine, Cd–NH_3 and Cd–$(NH_3)_2$.[20] We could explain theoretically the relation between the coordination number and the peak wavelength of the emission. In this paper we investigate the reaction mechanism in detail for the Cd–NH_3 and Hg–NH_3 exciplexes.

Calculation Method

We employed the relativistic effective core potentials developed by Christiansen and co-workers,[21,22] with the valence shells being 5s5p4d for the Cd atom and 6s6p5d for the Hg atom. The associated valence basis functions of 3s3p4d for the Cd atom and 3s3p4d for the Hg atom were used without contraction. We added a basis function augmented by a diffuse p-function (α_p = 0.012 74) on the Cd atom to describe the Rydberg orbital and α_p = 0.020 48 on the Hg atom. For other atoms, we used the 6-31G** basis set. The metal atom lies on the C_3 axis away from the H atoms. The geometry optimizations were carried out under C_s symmetry for these molecules. As a reaction coordinate, we chose the distance between the Cd or Hg atom and the N atom, R(Cd—N) or R(Hg—N). Molecular structures were optimized by changing R(Cd—N) or R(Hg—N). These calculations were carried out using the restricted Hartree–Fock (RHF) method for the ground state and the unrestricted Hartree–Fock (UHF) method for the first excited state. The geometry optimizations for the second-order Møller–Plesset perturbation calculation (denoted MP2)[23] were also carried out. Using the optimized parameters obtained above, the fourth-order MP calculations (denoted MP4) were carried out to evaluate the total energy.

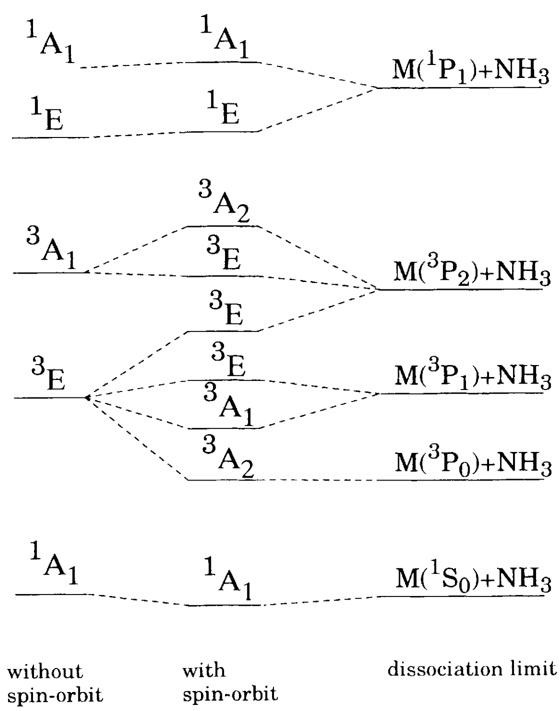

Fig. 1 Schematic correlation diagram of the potential-energy surfaces for linear dissociation without and with the effects of spin–orbit coupling

Since the Hartree–Fock (HF) and MP calculations for the excited states are not the eigenstates for S,[2,24] we performed spin-projected MP calculations (denoted PMP4). All the geometry optimization and the MP calculations were performed using GAUSSIAN90[25] or GAUSSIAN92.[26]

The effects of spin–orbit coupling may be evaluated by perturbation theory for the light-atom system in which the effects are relatively small. For the heavy-atom system, however, they must be calculated by the variational method. The SOCI method is suitable for these conditions, and has been applied to several compounds.[27–30] In the present study, the SOCI calculations were performed with the COLUMBUS program package[31] with several extensions including the spin-independent graphical unitary group approach (GUGA).[32] For these calculations, the structure of the NH_3 molecule was optimized by using 6-31G** basis sets assuming C_{3v} symmetry. Thus, the total symmetry of the exciplexes was C_{3v}. The molecular orbital (MO) coefficients for the CI calculations were the ground-state self-consistent field (SCF) MO vectors; the singlet and triplet configuration state functions (CSFs) were generated with reference to the active space (8a′ 9a′ 10a′ 11a′ 12a′ 4a″ 5a″).[2]

Two kinds of calculation were performed. The first took all the single excitations from the references in the first-order CI (FOCI) scheme. About 58 000 CSFs were included for each symmetry in the double group C_s'. The second calculation used both single and double excitations from the references in the multi-reference single and double CI (MRSDCI) scheme. Inner d-electrons, however, were neglected so that the CSFs did not become too large. For this system, excitation from inner d-electrons is not important. In this case, *ca.* 149 000 CSFs were included. Most of the calculations were carried out by the 'contracted SOCI' method, where the total Hamiltonian including the spin-orbit part was diagonalized on the basis of the corresponding spin-free CI eigenvectors for the above-mentioned states (X^1A', $^{1,3}A''$, $^{1,3}A'$).

Results and Discussion

Calculations without the Spin–Orbit Interaction

As previously mentioned from the Cd–ethylenediamine complexes,[20] the orbital orientation of the cadmium or mercury atom differs in the singlet and triplet states of Cd–NH_3 and Hg–NH_3 complexes. As an example, for the Cd–NH_3 complex the dominant configuration is $5s^2$ in the singlet state; on the other hand, 5s5p is dominant in the triplet state. This has an important contribution to the bonding interaction as indicated in the potential curves (Fig. 2 and 3).

The optimized bond distances and bond angles of the Cd–NH_3 and Hg–NH_3 complexes are given in Table 1 for the triplet state using the HF and MP2 methods. The structure of NH_3 in the exciplex was roughly the same as that of the NH_3 molecule. R(Cd—N) and R(Hg—N) for the MP2 optimized geometries were shorter than those for HF. In the case of Hg–NH_3, for which experimental data of R(Hg—N) are available,[19] the MP2 results are closer to the experimental value than the results from HF.

Table 1 Equilibrium bond distances (in Å) and bond angles (in degrees) of the triplet state for Cd–NH_3 and Hg–NH_3

	HF opt.	MP2 opt.	exp.
R(CD—N)	2.452	2.381	
$R(N—H_1)$	1.001	1.013	
$R(N—H_2)$	1.002	1.015	
∠(Cd—N—H_1)	112.1	112.1	
∠(Cd—N—H_2)	110.2	110.2	
R(Hg—N)	2.522	2.536	2.2[a]
$R(N—H_1)$	1.000	1.030	
$R(N—H_2)$	1.001	1.030	
∠(Hg—N—H_1)	111.2	109.4	
∠(Hg—N—H_2)	109.7	109.4	

[a] Ref. 19.

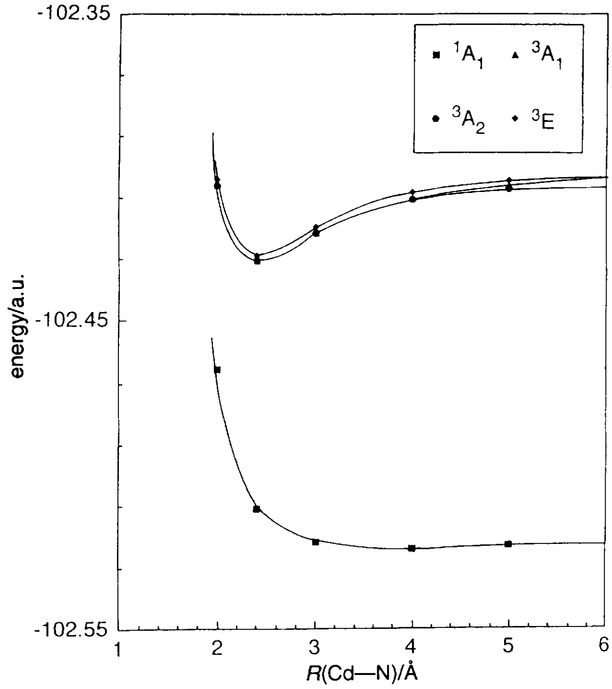

Fig. 2 Potential-energy curves for $^1A_1$, $^3A_2$, $^3A_1$ and ^3E states of Cd–NH_3, FOCI calculation

Table 2 lists the energy differences between the ground and first excited states for the exciplexes, which were assumed to have the same structure. These energy differences correspond to the wavelength of the emission from the experimental results. Generally, in the UHF calculation, the total energy is

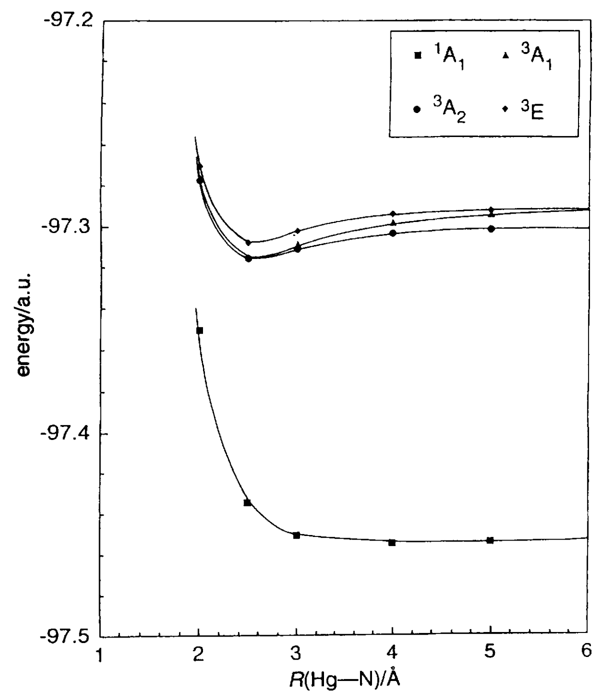

Fig. 3 Potential-energy curves for $^1A_1$, $^3A_2$, $^3A_1$ and ^3E states of Hg–NH_3, FOCI calculation

Table 2 Energy difference (in nm) between ground and first excited triplet states

	HF opt.			MP2 opt.			
	MP2	MP3	MP4	MP2	MP3	MP4	exp.
Cd–NH_3	510.2	491.3	477.8	530.5	507.7	493.1	450
Hg–NH_3	333.3	325.7	322.8	363.8	355.8	352.1	340

lower than that of the real triplet state because of spin contamination.[24] Therefore, in order to calculate the energy for the pure triplet state, the calculation is performed with the higher spin multiplicity term taken out. The energy difference in Table 2 is the value between these two states, which shows that the difference becomes larger with the degree of perturbation. It appears that the calculated results are in good agreement with experimental data despite the effects of spin–orbit coupling not being included.

The binding energy for the triplet state is listed in Table 3. Our results are much higher than the experimental value for the Hg–NH_3 exciplex.

Calculations including the Spin–Orbit Interaction

The total energy for the X^1A_1, $^3A_2$, $^3A_1$ and ^3E states from the SOCI calculation and excitation energies from the ground state are listed in Table 4. All the excitation energies from the ground state are lower than the results without the inclusion of the spin–orbit interaction. The origin of the discrepancy between the energy difference with the spin–orbit interaction and that without it may be due to the fact that the geometries of the calculated exciplexes were not optimized and that the correlation energy differed between the ground and the excited states. These energies also became larger as the number of CSFs increased. If larger CI calculations were to be done, the calculated results would be close to the experimental results.

The potential-energy curves calculated for the ground and several excited states of the Cd–NH_3 and Hg–NH_3 complexes are shown in Fig. 2 and 3. For Cd–NH_3, the energy splitting between the $^3A_2$ and $^3A_1$ state is very small. This result resembles that for a diatomic molecule such as CdXe. For the CdXe molecule, the $\sigma\pi$ $^3\Pi$ state splits to $^3\Pi_0$, $^3\Pi_1$, and $^3\Pi_2$ states owing to the effects of spin–orbit coupling, and the $^3\Pi_0$ state splits to $^3\Pi_{0-}$ and $^3\Pi_{0+}$ states from the second-order spin–orbit coupling.[33] As in our previous calculation,[34] the splitting between the $^3\Pi_{0-}$ and $^3\Pi_{0+}$ states of CdXe is very small, in analogy with Cd–NH_3. In the bonding region, this splitting is about 2.3 kJ mol^{-1}. The polarization from the N atom in Cd–NH_3 is larger than that from the Xe atom in CdXe. The splitting, however, originates from the Cd atom, so it is similar for Cd–NH_3 and CdXe. Most of the experiments on the photosensitized Cd–NH_3 reaction have been performed at >400 K because of the low vapour pressure of Cd. At high temperatures, fast transitions between these two states will occur. Thus, in experiment, it is difficult to distinguish between the two states.

Table 3 Binding energy (in kJ mol^{-1}) of first excited triplet states

	HF opt.			MP2 opt.			
	MP2	MP3	MP4	MP2	MP3	MP4	exp.
Cd–NH_3	88.97	86.24	90.28	91.22	86.61	90.80	
Hg–NH_3	93.43	86.95	92.94	93.81	84.94	92.58	66.99[a]

[a] Ref. 19.

Table 4 Total energy (in E_h[a]) from the SOCI calculations and (in parentheses) energy difference (in nm) from the ground states of the Cd–NH_3 and Hg–NH_3 complexes

	$CdNH_3$		$HgNH_3$	
	FOCI	MRSDCI	FOCI	MRSDCI
$X\,^1A_1$	−102.511 016	−102.523 339	−97.434 798	−97.443 779
$^3A_2$	−102.431 123	−102.435 535	−97.316 286	−97.318 591
	(570.3)	(518.9)	(384.5)	(364.0)
$^3A_1$	−102.431 064	−102.435 463	−97.315 311	−97.317 416
	(569.9)	(518.5)	(381.3)	(360.6)
^3E	−102.429 216	−102.433 436	−97.308 723	−97.310 087
	(557.0)	(506.8)	(361.3)	(340.8)

[a] 1 $E_h = 4.359\,748\,2\,(26) \times 10^{-18}$ J.

Summary

As an application of a quantum chemical calculation to cadmium- or mercury-photosensitized reactions, we investigated the emission from exciplexes of the Cd–NH_3 and Hg–NH_3 systems. For Hg–NH_3, the wavelength of the emission bands and the molecular structure were in good agreement with the experimental results. The splitting from the spin–orbit interaction for Cd–NH_3 was too small to distinguish between the emission states $^3A_1$ and $^3A_2$. From group theoretical considerations, however, it is thought that the emission occurs from $^3A_2$ in these systems.

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