verse magnetic susceptibility is fitted excellently to a straight line in the temperature range 10-269 K. The susceptibility exhibts typical Curie law depedence, with the Curie constant of 1.014 emu K mol^{-1}.

Acknowledgement. This work was supported by a grant from the Basic Research Institute Program (1992), Ministry of Education, Republic of Korea.

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Valence States of SH^{2+} by *Ab Initio* Effective Valence Shell Hamiltonian

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Received June 19, 1992

Recently the electronic states of doubly positive diatomic cations have been investigated extensively[1,2]. In those studies a few quasibound states of doubly positive diatomic cations have been found. There is a repulsive force between two singly positive monatomic cations. The repulsive force is overcome sometimes by redistribution of electron densities when a doubly positive diatomic cation is formed. Therefore metastable bound states can exist in some cases. In other words the avoided curve crossing between a state arising from an ion-ion asymptote (dissociation limit) and a state with the same symmetry arising from an ion-neutral asymptote is a main reason for the existence of quasibound states in doubly positive diatomic cations.

We have studied the nature of the effective valence shell Hamiltonian (H^v) which is based on the quasidegenerate many-body perturbation theory[3]. One of remarkable features of H^v is that the effective H^v operator can reproduce all the valence states of a neutral molecule and its ions simultaneously regardless of its charge states. Once the matrix elements of H^v are evaluated for a neutral molecule, the same matrix elements can be used to determine the valence states of its singly positive, doubly positive,⋯ cations.

The existence of the bound states in NO^{2+}, O_2^{2+}, etc. may be easily predicted. But for the first row diatomic monohydrides, say, CH^{2+}, or NH^{2+} cation, the existence of unusually stable states may not be easily understood. If two electrons are removed from the $1\pi^2$ orbital of neutral NH, NH^{2+} may exist because the 1π orbital of neutral NH has basically nonbonding character. For CH^{2+}, the prediction of its existence is not so simple because at least one electron should be removed from a bonding 3σ orbital of neutral CH to form CH^{2+} cation. We have previously studied the CH^{2+} cation and found no bound states.[4] Therefore so far the H^v has been mainly applied to neutral molecules and singly positive cations. But recently doubly positive cations of various second row diatomic monohydrides have been studied by configuration interaction (CI) method[5,6]. We are encouraged by these studies so that now we apply the H^v method to these systems.

In the present work, we have performed H^v calculations on the SH^{2+} cation. The SH^{2+} cation has been studied previously[2,6]. But one should note that a single H^v calculation simultaneously produces all the valence state energies with same accuracy. So that our present H^v calculations reveal a composite picture of the SH^{2+} potential energy curves of all the valence states.

The second order effective valence shell Hamiltonian calcalculations for SH^{2+} are performed with a contracted Gaussian basis set of $[7s5p3d]$ for sulfur and $[2s1p]$ for hydrogen[7]. Molecular orbitals are obtained from the SCF (self-consistent-

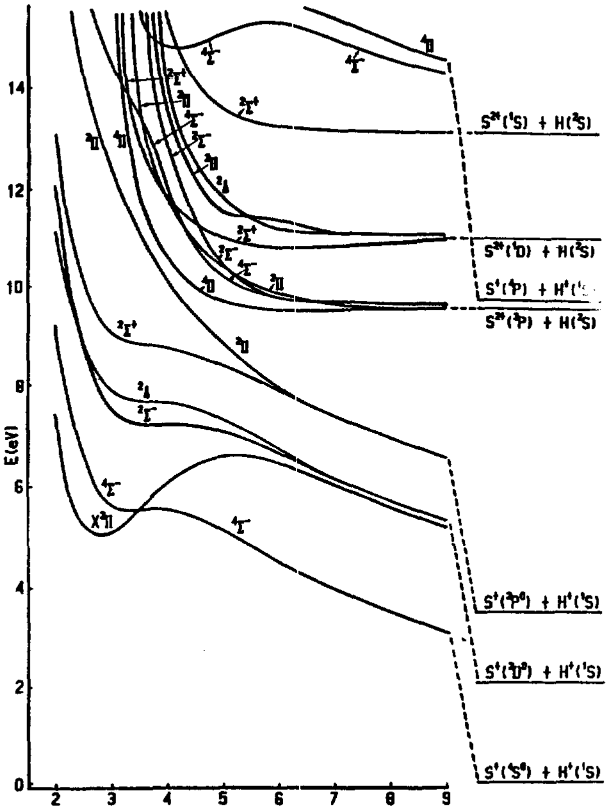

Figure 1. Adiabatic potential energy curves of SH^{2+}.

Table 1. Deprotonation Energy, Activation Energy Barrier and Spectroscopic Constants for the $X^2\Pi$ State of SH^{2+}

	H^v	HF[a]	CASSCF[b]	MRDCI[a]	CI+ZPVE[c]
Deprotonation energy (eV)	−2.95	−3.32	−3.11	−2.92	−3.02
	H^v	HF[a]	CASSCF[b]	MRDCI[a]	CI+ZPVE[c]
Activation-energy barrier (eV)	1.58	1.70	1.52	1.67	1.57
Spectroscopic constants	R_e (au)	ω_e (cm^{-1})	$\omega_e\chi_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})
H^v	2.744	2050	99.3	8.10	0.19
CASSCF[a]	2.742				
$CASSCF_b$	2.733	2023	57.4	8.25	0.27

[a] Ref. 6, [b] Ref. 2, [c] Ref. 6 with zero point correction.

field) calculation for the ground $^2\Pi$ state of SH^{2+}. 1σ, 2σ, 3σ, $1\pi_x$, and $1\pi_y$ orbitals are chosen as core orbitals and 4σ, 5σ, $2\pi_x$, $2\pi_y$ and 6σ orbitals are as valence orbitals which come from 3*s* and 3*p* of sulfur and from 1*s* of hydrogen. All the other remaining orbitals are classified as excited orbitals. The orbital energies are taken from SCF orbital energies and to guarantee a fast convergence, the orbital energies of valence orbitals are arithmetically averaged. With this choice, the matrix elements of H^v are evaluated at various internuclear distances, *i.e.*, 2.0, 2.25, 2.5, 2.55, 2.6, 2.75, 2.85, 3.0, 3.5, 4.0, 4.5, 5.0, 6.0, 7.0, 8.0, and 9.0 au. The 8th degree polynomial expansion is used to fit the bound state potential energy curve to have Dunham coefficients, which give the various spectroscopic constants. The asymptote is determined from separate H^v calculations for monatomic S^+ and S^{2+}. H^+ has zero electronic energy and neutral *H* has exactly −0.5 au of electronic energy.

As shown in Figure 1, the ground $^2\Pi$ state is found to be quasibound (metastable). Its bond length is 2.744 au and the activation energy barrier is 1.58 eV. Emanating from the ion-neutral pair asymptote of $S^{2+}(^3P)+H(^2S)$, there are four states, *i.e.*, $^{2,4}\Sigma^-$ and $^{2,4}\Pi$ states. As in Miller *et al.*'s CI calculations[2], these states are found to be not quasibound. Slightly above this asymptote there is the ion-ion pair asymptote of $S^+(^4P)+H^+(^1S)$ which gives the $^4\Sigma^-$ and $^4\Pi$ states. Therefore one expects that there should be strong interaction between the $^4\Sigma^-$ (or $^4\Pi$) state from the $S^{2+}(^3P)+H(^2S)$ asymptote and that from the $S^+(^4P)+H^+(^1S)$ asymptote so that a quasibound $^4\Sigma^-$ (or $^4\Pi$) state is formed. In reality, our H^v calculations reveal that the $^4\Sigma^-$ and $^4\Pi$ states from $S^+(^4P)+H^+(^1S)$ are strongly repulsive even at very large internuclear distances. Thus there are no interactions between these two kinds of the $^4\Sigma^-$(or $^4\Pi$) states. The $^2\Pi$ state from $S^{2+}(^1D)+H(^2S)$ has a shallow minimum, which seems to be due to the avoided curve crossing between the $^2\Pi$ state from $S^{2+}(^3P)+H(^2S)$ and the $^2\Pi$ state from $S^{2+}(^1D)+H(^2S)$. As we see in Figure 1, this quasibound state is not caused by the interaction of a repulsive state from an ion-ion pair asymptote with the same symmetry state from an ion-neutral pair asymptote.

Table 1 presents a comparison of H^v results with other theoretical values. The deprotonation energy, which is an energy difference between the asymptote of $S^+(^4S^\circ)+H^+(^1S)$ and the $X^2\Pi$ state of SH^{2+} at equilibrium, is calculated as −2.95 eV. The spectroscopic constants which represent the well shape of the $X^2\Pi$ quasibound state, are also compared. Generally our H^v values are in very good agreement with other theoretical CASSCF or CI values.

Here we have reconfirmed the validity of the effective valence shell Hamiltonian method. Specifically it is shown that H^v reproduces all the repulsive and quasibound valence states of doubly positive SH^{2+} cation. Compared with our previous H^v studies on SH and SH^+, it is also confirmed that the same set of matrix elements of H^v can be used for a neutral molecule and its doubly positive cation which has two less number of electrons than the corresponding neutral species[8]. Full results will be reported in the near future.

Acknowledgement. This work has been supported by the Korea Science and Engineering Foundation through the Center for Molecular Science. The support from PNU Research Fund is also acknowledged.

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Facile Synthesis of 4-N-Benzoyl-5-bromo-2′-deoxycytidine

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Received July 13, 1992

Several 5-halopyrimidines, their ribosides and deoxyribosides, have interesting inhibitory effects upon growth of bacteria, bacteriophage, molds and tumors. Some of these antimetabolites inhibit thymidine synthesis, others prevent thymidine utilization, and depending to some extent on the size of the halogen[1,2], the abnormal pyrimidine may be incorporated into RNA or DNA[3]. In addition to the possible usefulness of these derivatives in the studies of nucleic acid metabolism, genetics and as chemotherapeutic agents, these compounds are potential replacements for 5-methyl-2′-deoxycytidine found in some plants and animal DNA and 5-hydroxymethyl-2′-deoxycytidine in the coliphage DNA of the even varieties[4]. The unusual important activities of the above derivatives initiated many workers to participate in studies of these compounds.

For studies on the mechanism of restriction endonuclease catalyzed reactions and on drug-DNA interaction, we were forced to synthesize 4-N-protected-5-bromo-2′-deoxycytidine as a building block for synthesis of oligodeoxyribonuclotides which contain 5-bromo-2′-deoxycytidine. In this note we report the facile synthesis of 4-N-benzoyl-5-bromodeoxycytidine and its derivative.

Results and Discussion

It seemed likely that we would first prepare 5-bromo-2′-deoxycytidine by using the reported procedure[4,5] and then protect 4-N-exocyclic amino group to 5-bromo-2′-deoxycytidinewith appropriate protecting group[6]. We, therefore, treated 2′-deoxycytidine with bromine in dry pyridine using the reported procedure[4]. The reaction mixture showed several spots on TLC and the reported procedure appeared to be impractical. It seemed that it would be necessary to use fully protected 2′-deoxycytidine for the bromination. Our first choice of the fully protected deoxycytidine was 4-N-3′,5′-O-tribenzoyl-2′-deoxycytidine. 4-N-3′,5′-O-tribenzoyl-2′-deoxycytidine was converted to 5-bromo derivative with bromine in satisfactory yield (70%). After the product was purified by short column chromatography, the product was treated with NaOMe for removing of 3′,5′-O-dibenzoyl groups to give 4-N-benzoyl-5-bromo-2′-deoxycytidine 1. Surprisingly, it was depyrimidinated completely. It was probably due to bromo-substituent of 2′-deoxycytidine which has electron withdrawing property. Thus, our next starting material was 4-N-protected-2′-deoxycytidine, 4-N-benzoyl-2′-deoxycytidine 3, which was treated with bromine and yielded many products on TLC. But when we changed bromine for N-bromosuccinimide, it has been found that bromination of 4-N-benzoyl-2′-deoxycytidine was conveniently accomplished in practical yield (52%).

Derivatization of the 5′-hydroxy group of 4-N-benzoyl-5-bromo-2′-deoxycytidine 1 was achieved by treatment of 4-N-benzoyl-5-bromo-2′-deoxycytidine 1 with 9-chloro-9-phenylxanthene (pixyl chloride) in pyridine by following the reported procedure[7]. Alternatively, 5′-pixyl-4-N-benzoyl-2′-deoxycytidine 4 was allowed to react with N-bromosuccinimide in pyridine in a manner analogous to that described for bromination of N-benzoyl-2′-deoxycytidine 3 and converted to the 4-N-benzoyl-5-bromo-5′-O-pixyl-2′-deoxycytidine 2 as outlined in Figure 1. Both procedures gave the 4-N-benzoyl-5-bromo-5′-O-pixyl-2′-deoxycytidine 2 in good yield.

The stabilities of the titled compound and its pixyl derivative were tested under various conditions which are applied in oligodeoxyribonucleotide synthesis[8]. They are stable enough to be used as building blocks. Thus, the titled compound and its pixyl derivative are safely using as building blocks in the synthesis of oligodeoxyribonucleotides which contain 5-bromodeoxycytidine in this laboratory.

Experimental

^{1}H-NMR spectra were measured with a Bruker 300 MHz spectrometer. TLC was carried out on Merck silica gel 60F$_{254}$ plates. Merck silica gel H was used for short column chromatography[9]. Pyridine was dried by refluxing with calcium hydride and was then distilled at atmospheric pressure.