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Abstract

The isotope effect induced by deuterium substituted species is observed in molecular properties, such as geometry, kinetics, and electronic state of the molecules through nuclear-electron interaction. Theoretical considerations and experimental alignments have been studied by *ab initio* molecular orbital (MO), density functional (DF) theory, and other empirical strategies. The Born-Oppenheimer (BO) approximation with nuclear vibrational wavefunction can treat isotope effect because nuclear mass effect account for the average distance of vibrational motion. In this study, we introduce Morse anharmonic oscillator model to calculate *average* internuclear

distance of diatomic molecules having X-H bonding and X-D bonding. Morse parameters are determined by fitting to potential energy surface of MO and/or DF calculations, then the average distance are obtained as the expectation value of the analytical Morse vibrational wavefunction. NMR shielding constants of the H/D isotopomer are calculated again on the average distance by using GIAO with B3LYP and CCSD calculation.

Keywords: isotope effect; NMR shielding constant; Morse oscillator; vibrationally averaged property; thermal average

1. Introduction

The isotope effect induced by deuterium substituted species is observed in molecular properties, such as geometry, kinetics, and electronic state. It is caused by the geometrical and kinetic changes to molecular property through nuclear-electron interaction. Isotope effects on magnetic properties such as nuclear magnetic resonance (NMR) chemical shifts and coupling constants are also important to determine molecular structures with deuterium labeled [1]. Theoretical considerations and experimental alignments have been studied by *ab initio* molecular orbital (MO), density functional (DF) theory, and other empirical strategies. The Born-Oppenheimer (BO) approximation with nuclear vibrational wavefunction can treat isotope effect because nuclear mass effect account for the average distance of vibrational motion partially. On the other hand, exact solution should be discussed beyond the BO framework. Recently, one of the way to include nuclear quantum effect to electronic structure calculation, multi-component quantum

chemical theory [2, 3, 4] has been available to describe nuclear wavefunction and electronic wavefunction simultaneously, even in deuterium isotope effect [5, 6, 7]. However, the computational costs are too expensive to solve large system and all isotopes are not studied well.

Empirically, the theory of nuclear vibration effect has been developed with formulation of zero-point vibration [8], thermodynamical correction [9]. *Ab initio* approaches based on potential energy surface (PES) have also proposed as combination of nuclear vibrational states of anharmonic potential with Gauge-Independent Atomic Orbital (GIAO) method [10] to determine isotope shifts of NMR shielding parameters [11, 12, 13]. In the above studies, the shapes and the characters of PES and magnetic shielding surface (MSS) discussed with relation to thermal nuclear vibrational motion and the isotope effect. Moreover, beyond normal mode analysis based on harmonic oscillator, several ways are proposed theoretically. One of the method is based on zero-point vibrational correction (ZPVC) expanding to high-order term by Taylor series by Ruud and co-researchers [14, 15]. Another is quantum dynamics method using nuclear wavepacket dynamics [16] running on quantum-chemical or empirical PESs, or path-integral Monte Carlo (PIMC) approaches with many samplings [17, 18] have been proposed.

The calculations based on PES, and normal mode analysis certainly consider the anharmonicity of nuclear vibration for molecular system, and the isotope effect for the kinetics and the molecular properties. On the other hand, considerable degrees of freedom of normal modes in those approaches, which is rather low-cost than PIMC and the

3

wavepacket. The wavepacket method and PIMC show exact results depended on the pre-obtained PES or the number of samplings. However, they are too time-consuming especially in large molecular system.

The paper will focus on development of approximated way to solve both vibrationally averaged properties, especially of NMR and their thermal averages. As the first steps of the objective, we introduce Morse anharmonic oscillator model to calculate *average* internuclear distance of diatomic molecules having X-H bonding and X-D bonding. Morse parameters are determined by fitting to PES of MO and/or DF calculations, then the average distances are obtained as the expectation value of the analytical Morse vibrational wavefunctions. NMR shielding constants of the H/D isotopomer are calculated again on the average distance by using MO- and DF-GIAO method.

2. Theory and Computational Details

2.1 Vibrationally averaged structure and shielding constant

Generally the averaged shielding constant can be expressed by the shielding constant at the equilibrium structure and derivatives with respect to internuclear bond lengths and angles [19]. First, we define the set of equilibrium bond length $\mathbf{R}_{eq}$. Now we introduce new set of bond length $\mathbf{R}$ in which the bond length of isotope is replaced by averaged one $\langle R \rangle$. The following procedure, $\langle \sigma \rangle$ means $\sigma(\mathbf{R})$ which is shielding constant calculated by using $\mathbf{R}$.

Second, we apply Morse potential [20] as anharmonic oscillator according to proce-

dure by Dios and Jameson [11, 12]. Once potential is determined, an effective behavior of

the anharmonic vibration is reproduced as the forms of nuclear vibrational wavefunction

analytically. The nuclear and the electron of the system is defined as

$$\Phi(\mathbf{r}; \mathbf{R}) \approx \chi(\mathbf{R})\phi(\mathbf{r}; \mathbf{R}) \tag{1}$$

$$\hat{H}_{\text{elec}}\phi(\mathbf{r}; \mathbf{R}) = U\phi(\mathbf{r}; \mathbf{R}) \tag{2}$$

where Φ, χ, and ϕ are the total wavefunction, the nuclear wavefunction, and the elec-

tronic wavefunction with nuclear coordinate $\mathbf{R}$ and the electronic coordinate $\mathbf{r}$, respec-

tively. U means adiabatic potential along with fixed-nuclei coordinates. Under the BO

approximation, nuclear wavefunctions are depended on U and the potential has anhar-

monic shape function, which is very similar to Morse potential. The nuclear coordinate

is one-dimensional in the case of diatomic molecule, i.e.,

$$V_{\text{M}}(R) = D_{\text{e}}\big(1 - e^{-\alpha(R - R_{\text{e}})}\big) \tag{3}$$

where parameters D_{e}, α, and R_{e} mean a dissociation energy, a force constant, and an

equilibrium internuclear distance, respectively. The Morse parameters are determined

by fitting to PES obtained by *ab initio* MO or DF calculation in this study. One can also use

spectroscopic data for the parameters. Applying Morse potential has a great advantage

in computational cost, because one can obtain analytical form of Morse wavefunction in

stead of solving rotation-free nuclear Schrödinger equation

$$\big(T_{\text{vib}}(R) + U(R)\big)\Psi_{\text{vib}} = E\Psi_{\text{vib}} \tag{4}$$

where Ψ_{vib} is vibrational wavefunction and T_{vib} is kinetic operator for nuclear motion.

The solution of Ψ_{vib} has only Laguerre polynomials with normalized factors, and con-

tains ground and excited vibrational states simultaneously [20]. Finally we can obtain averaged internuclear distance $\langle R \rangle$ as expectation value

$$\langle R \rangle = \langle \Psi(R)|R|\Psi(R) \rangle. \tag{5}$$

Practically we calculate the analytical function Ψ and Eqn.(5) in the numerical discrete variable representation (DVR) of 0.0001 a.u. (0.1 mBohr) grid. The computational implementation has been used in our previous studies for multiphoton process between vibrational levels of diatomic molecule in detail [21, 22]. We also check the Cooley-Numerov method [23] and Fourier Grid Hamiltonian (FGH) method [24]. Analytical solution in this study is even more effective because it has no diagonalization steps and the computational time is only several seconds with the large grid points. This advantage becomes important to extend for polyatomic system in the future work.

2.2 Ab initio and density functional calculation for PES and MSS

For the prediction of NMR shielding constant, Gauge-Independent Atomic Orbital (GIAO) method [10, 25] has been developed with Hartree-Fock (HF), the 2nd order Møller-Plesset perturbation theory (MP2), coupled-cluster (CC), and Density Functional Theory (DFT). In particular, DFT has been chosen to calculate the electronic and geometrical structure of chemical / biochemical molecular systems because of lower computational cost and reliability, also in the NMR prediction [26, 27] whereas MP2 and CC approaches have higher cost and systematically improvement of the agreement with experimental values [28, 29].

In DF calculation, we use Becke's three parameter exchange functional [30] and

the Lee-Yang-Parr correlation functional [31] (B3LYP), and parameter-free functionals proposed by Perdew, Ernzerhof and Burke [32, 33] with 25% exchange term so called PBE1PBE [34], which are formulated by adiabatic connection method (ACM) [35]. PES and GIAO calculation by using HF, MP2, and DF are performed in Gaussian 03 program suite [36]. In CC calculation, coupled-cluster singles and doubles (CCSD) is applied for PES and GIAO calculation in CFOUR version 1.2 developed by Stanton *et al.* [37]. All of calculations are performed as unrestricted open-shell treatment with Dunning's correlation-consistent triple-ζ valence basis set added diffuse functions, aug-cc-pVTZ.

2.3 Thermal average at finite temperature

After solving nuclear vibrational wavefunction, we calculate thermal averaged distance by using Boltzmann's distribution

$$\langle R \rangle^T = \frac{\sum_\nu e^{-E_\nu/k_{\mathrm{B}}T} \langle \Psi_\nu(R)|R|\Psi_\nu(R)\rangle}{\sum_\nu e^{-E_\nu/k_{\mathrm{B}}T}} = \sum_\nu n_\nu \langle R \rangle_\nu \tag{6}$$

where Ψ_ν means ν-th vibrational wavefunction, k_{B} is the Boltzmann constant, and T is temperature in K, respectively. As the result of the thermal average, the average distance $\langle R \rangle^T$ at finite temperature T is made of the coefficients n_ν corresponding to the population probability of the ν-th vibrational level. Finally we obtain thermal averaged NMR shielding constant at the distance $\langle R \rangle^T$ by similar definition

$$\langle \sigma \rangle^T = \frac{\sum_\nu e^{-E_\nu/k_{\mathrm{B}}T} \sigma\big(\langle \Psi_\nu(R)|R|\Psi_\nu(R)\rangle\big)}{\sum_\nu e^{-E_\nu/k_{\mathrm{B}}T}} = \sum_\nu n_\nu \sigma\Big(\langle R \rangle_\nu\Big). \tag{7}$$

2.4 Primary isotope effect and target molecules

We apply the above procedure to diatomic molecules and the deuterated isotopes, H_2 and HD as homo-nuclear molecules, HCl and DCl, NaH and NaD as hetero nuclear systems. MO- and DF-GIAO calculations are performed to obtain ^{1}H-, [35]Cl-, ^{23}Na-NMR shielding constant as isotropic value $\sigma_{\mathrm{iso}} = \frac{1}{3}(\sigma_{xx} + \sigma_{yy} + \sigma_{zz})$. Deuterated isotopes does not have ^{1}H-NMR shielding without HD molecule, hence the isotope effect appears on the D-bonded atoms. We can obtain NMR isotope shift between H/D isotopomers as

$$^1\Delta = \langle\sigma\rangle_{\mathrm{XD}}^T - \langle\sigma\rangle_{\mathrm{XH}}^T \tag{8}$$

where X = H, Cl, and Na, corresponding to isotopomers. The index "1" means distance from deuterium binding atom, we then treat the primary shift only in the case of diatomic molecules. We apply GIAO/B3LYP/aug-cc-pVTZ by Gaussian 03 [36], and GIAO/CCSD/aug-cc-pVTZ by CFOUR [37] to calculate NMR shielding constant and isotope shift.

3.   Results and Discussion

3.1   PES and MSS

We now test the behavior of PES which determines the shapes of the nuclear wavefunction and MSS which affects the NMR isotope shift between H/D-isotopomers. Figure 1 shows PESs of H_2 molecule calculated by using five different levels of MO and DF calculation, UHF, UB3LYP, UPBE1PBE, UMP2, and UCCSD with aug-cc-pVTZ basis set.

The PESs show underestimated dissociation energy in HF. In the middle range from 1.0 Å to 2.0 Å, MP2 result becomes upper than the energy of B3LYP and PBE1PBE which converge toward UCCSD. MSSs also show isotropic values of ^{1}H-NMR shielding surfaces of H_2 in Fig.1. All of curves show similar deshielding character along to molecular dissociation. HF result becomes lower than the others, however, the difference is quite small within 0.5 ppm.

For HCl molecule, Figs. 2(a) and (b) show PESs and ^{1}H- and ^{35}Cl-NMR shielding surfaces, respectively. Two DF energies of UB3LYP and UPBE1PBE are less than MP2 and CCSD results, and dissociation energy of HF is underestimated similar to H_2. Both MSSs in Fig. 2(a) and (b) provide deshielding on nuclear poles as same as H_2. NaH results are shown in Figs. 3 (a) and (b). The characters of PESs are very similar to HCl results. On the other hands, ^{23}Na surfaces show shielding property along to large distance more than 1.0 Å, whereas the surfaces less than 1.0 Å have minima.

The opposite direction of shielding surface between HCl and NaH implies that after molecular dissociation the atomic electronic density on the nuclei becomes increase or decrease, in other words, Cl becomes anionic and Na becomes cationic state on the contrary. Thus, the direction of isotope shift depends on ionic state of the dissociation state. The average distance extend to dissociation when the molecule has a lighter isotope. Heavier isotope case is *vice versa*.

The characters of PES in hetero nuclear molecules, HCl and NaH are not systematically improved in DF calculations. B3LYP and PBE1PBE can represent the shape of CCSD results although their potential energy are lower than CCSD results. We then

apply PES of CCSD to determine Morse parameters in the following subsections.

3.2 Morse parameters and Averaged internuclear distances

From CCSD/aug-cc-pVTZ results of PES, we determine Morse parameters by least square fitting. Table 1 summarizes three Morse parameters R_e, α and D_e. These parameters are exact same in isotopes under BO approximation. The difference of reduced mass between H and D appears the number of vibrational levels. ν_{max} of XD becomes less than one of XH. We then calculate Morse nuclear wavefunctions $\Psi(R)$ using these parameters and the expectation values as average internuclear distances as shown in Table 2. Both $\langle R_{XH} \rangle$ and $\langle R_{XD} \rangle$ extended slightly from equilibrium distance R_e. The ratios of isotope effect in internuclear distances to R_e are small from 1.1 % to 3.0 %.

Next, we apply Eqn.(6) to get the thermal average at finite temperature T = 300 K. The average $\langle R \rangle$s have little extension because the population of excited vibrational states is very small, that is, almost probabilities of vibration are located on ground state.

As shown in Table 3, the isotope shifts of internuclear distance $\Delta \langle R \rangle$ are obtained by $\langle R_{XD} \rangle - \langle R_{XH} \rangle$ with multi-component quantum chemical theory [6] and CCSD/aug-cc-pVTZ with anharmonic ZPVC correction [14] by using anharmonic driver of CFOUR. The results of ground vibrational state are good agreements with each method even later contains no excited vibrational states. Applying thermal average by Eqn.(6), the results $\langle R \rangle^T$ is decreasing slightly toward good agreement.

3.3 Shielding constants at averaged distances and isotope shifts

Finally we evaluate the isotope shift of NMR shielding constant by using thermal average internuclear distance $\langle R \rangle^T$. We assume T = 300 K as a room temperature. Table 4 summarizes NMR-GIAO shielding constant $\sigma(R_{\mathrm{e}})$, thermal averaged σ^T by Eqn.(7), and the primary isotope shift by Eqn.(8). The result of ^{1}H isotope shift agrees with the order of experimental results [38, 39, 40]. It shows CCSD contribution to B3LYP is only 0.001 ppm in isotope shift. [35]Cl- and ^{23}Na-NMR shielding constants become larger value than ^{1}H, thus, the magnitudes of isotope shift are 3–4 ppm and -0.5 ppm, respectively. As previous discussion in subsection 3.1, the shielding or deshielding trend determine the sign of $^1\Delta$. We have small differences between B3LYP and CCSD results in both [35]Cl and [23]Na, 0.1–1 ppm in $^1\Delta$. If one want to treat isotope shift of heavy element, electron correlation should be considered for GIAO calculations.

4. Concluding Remarks

In this study, we have calculated primary isotope shifts of NMR chemical shift of diatomic molecules. Isotope effect has been teated at the average distance, not at the equilibrium distance. The average distances have been obtained by using Morse oscillator and their nuclear vibrational wavefunctions by fitting to PES of UCCSD/aug-cc-pVTZ. The shielding tensors have been also calculated by GIAO/CCSD/aug-cc-pVTZ.

The characters of MSS represents the feature of shielding around the equilibrium distance. Deshielding or shielding characters are depended on the ionic state of dissociation state. Thermal averages have been also calculated at T = 300 K, however, there are no significant difference between 0 K and 300 K. The quite small widths of excited vibrational levels show small differences in the systems. By using Morse oscillator, isotope effect of H/D are effectively obtained with low computational cost. B3LYP and CCSD results of shielding constant are quite close within the range of 1 ppm – 100 ppb.

In the future work, we will approach primary and secondary isotope shift of polyatomic molecule such as methane and benzene derivatives. It is required to extend multi-dimensional system with this approach. We then focus on only the averaged bond length involved with isotopes. For bending vibration and torsional vibration, another type of oscillator or treatment should be required.

Acknowledgment

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Table 1: Morse parameters determined by using CCSD/aug-cc-pVTZ, reduced mass of isotopomers, and the maximum number of the vibrational levels of isotopomers.

XH (XD)	R_e /Å	D_e /eV	α /Bohr^{-1}	μ_{XH} /amu	μ_{XD} /amu	$\nu_{max,XH}$ ($\nu_{max,XD}$)
H_2 (HD)	0.7430	4.8300	1.0715	925.3	1233.4	16 (19)
HCl (DCl)	1.2767	5.0921	1.1110	1798.7	3496.8	22 (32)
NaH (NaD)	1.9271	2.0925	0.5769	1772.8	3400.3	28 (39)

Table 2: Equilibrium internuclear distance R_e, average internuclear distance $\langle R_{XH} \rangle$ of hydrogen isotope, $\langle R_{XD} \rangle$ of deuterated isotope in Å, and their ratio to R_e. $\langle R \rangle^T$ denotes the thermal averaged distance at $T = 300$ K.

XH(XD)	R_e	$\langle R_{XH} \rangle$	$\langle R_{XH} \rangle^T$	$\frac{\langle R_{XH} \rangle}{R_e}$	$\langle R_{XD} \rangle$	$\langle R_{XD} \rangle^T$	$\frac{\langle R_{XD} \rangle}{R_e}$
H_2 (HD)	0.7430	0.7654	0.7654	1.030	0.7623	0.7623	1.026
HCl (DCl)	1.2767	1.2922	1.2922	1.012	1.2877	1.2877	1.009
NaH (NaD)	1.9271	1.9515	1.9517	1.013	1.9496	1.9453	1.009

Table 3: Differences of internuclear distance between H/D isotopomers.

| XH(XD)	0 K		300 K	
	Ours	MC[a]	Ours	CFOUR[b]
H_2 (HD)	-0.0031	-0.0067	-0.0031	-0.0033
HCl (DCl)	-0.0045		-0.0045	-0.0044
NaH (NaD)	-0.0068		-0.0064	-0.0062

[a]Nuclear and molecular orbital calculation by González *et al.* [6].

[b]Anharmonic zero-point vibrational correction [14] by using CCSD/aug-cc-pVTZ with CFOUR anharmonic driver.

Table 4: Calculated NMR-GIAO shielding constant σ in ppm at the equilibrium internuclear distance R_e, the average internuclear distance $\langle R_{XH}\rangle^T$ of hydrogen isotope, and $\langle R_{XD}\rangle^T$ of deuterated isotope. Primary isotope shift $^1\Delta$ is the difference between the shielding constant of the isotopomers at $T = 300$ K.

| Nucleus of molecule	B3LYP/aug-cc-pVTZ				CCSD/aug-cc-pVTZ				
	$\sigma(R_e)$	$\sigma^T(\langle R_{XH}\rangle)$	$\sigma^T(\langle R_{XD}\rangle)$	$^1\Delta$	$\sigma(R_e)$	$\sigma^T(\langle R_{XH}\rangle)$	$\sigma^T(\langle R_{XD}\rangle)$	$^1\Delta$	$^1\Delta_{exp}$
^{1}H of H$_2$ (HD)	26.699	26.262	26.321	0.059	26.663	26.221	26.281	0.060	0.036 - 0.040 [a]
^{1}H of HCl (DCl)	32.423	30.963	-	-	31.085	30.610	-	-	-
^{35}Cl of HCl (DCl)	948.255	936.135	939.622	3.527	972.478	962.048	965.076	3.028	
^{1}H of NaH (NaD)	25.831	25.743	-	-	25.969	25.883	-	-	-
^{23}Na of NaH (NaD)	577.492	579.484	578.952	-0.532	580.931	582.269	581.917	-0.353	

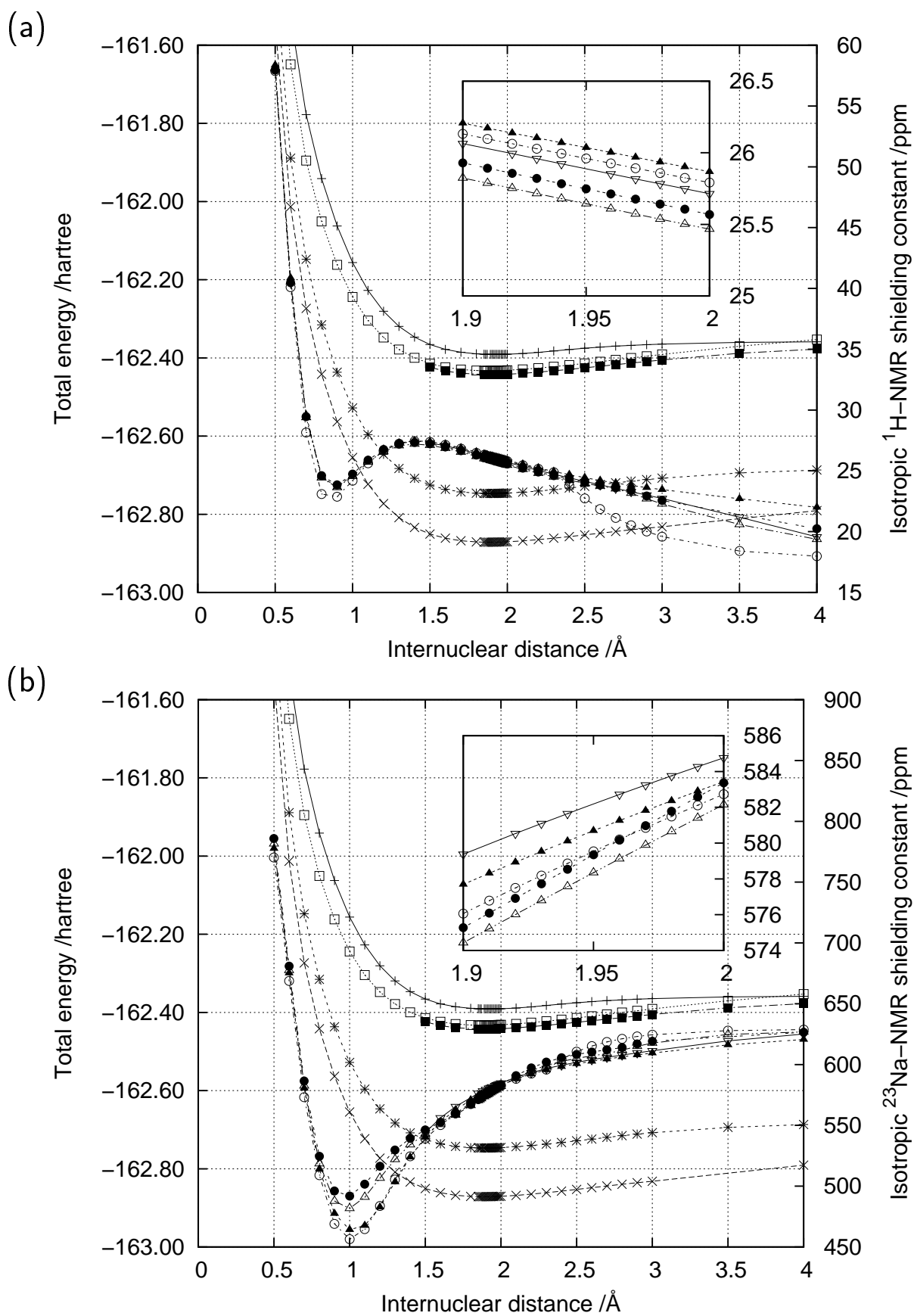[a] Experimental results at 300 K from Ref.[38, 39, 40].

Figure 1 K. Sugimori et al.

(a)

(b)
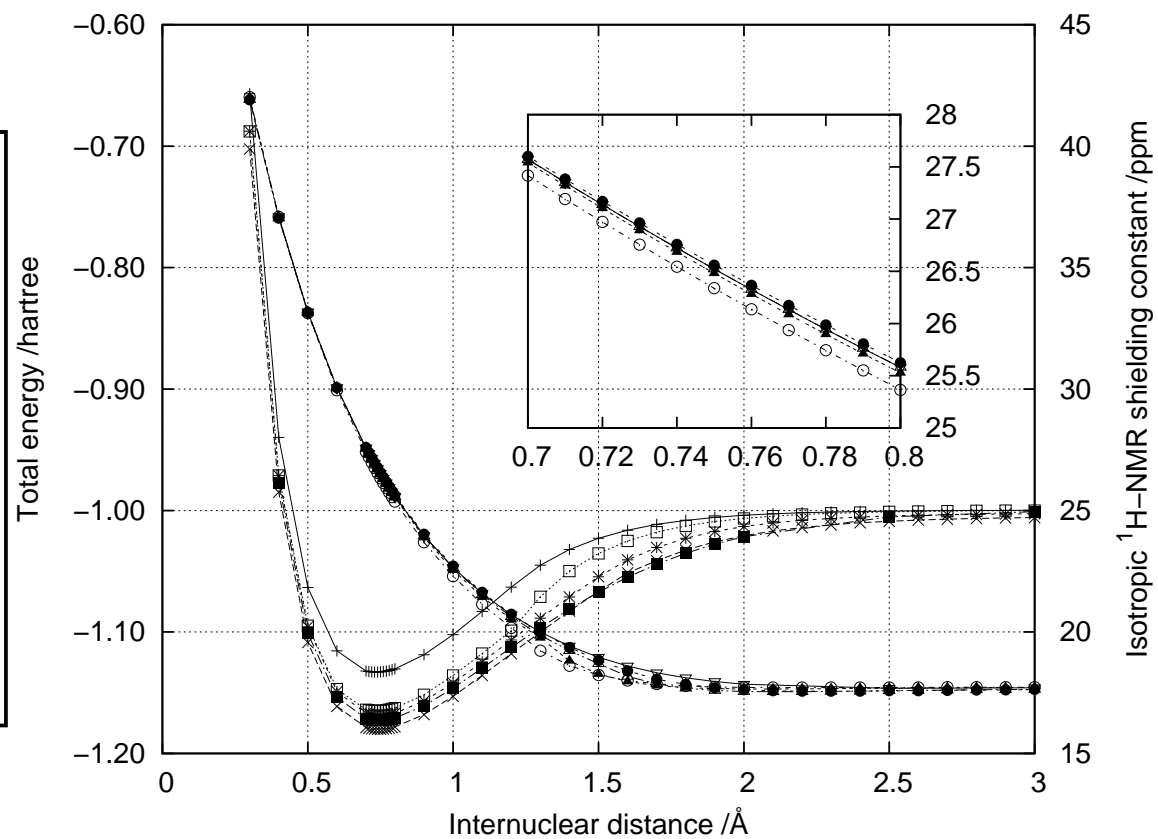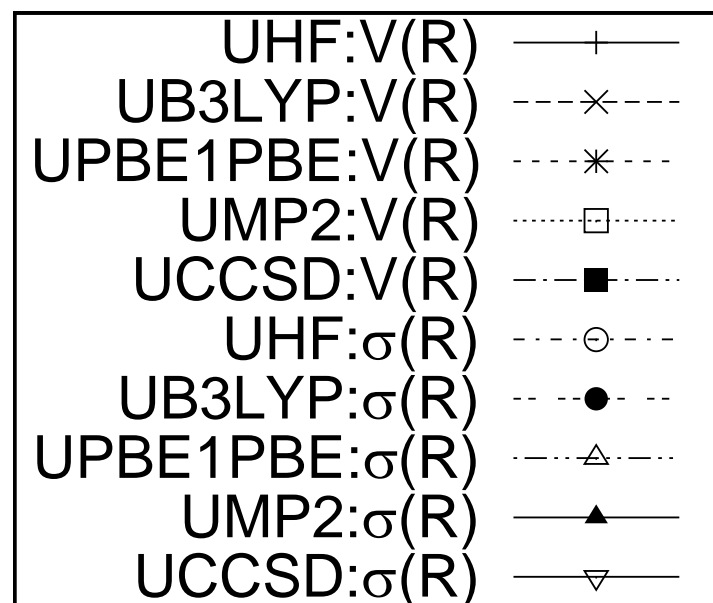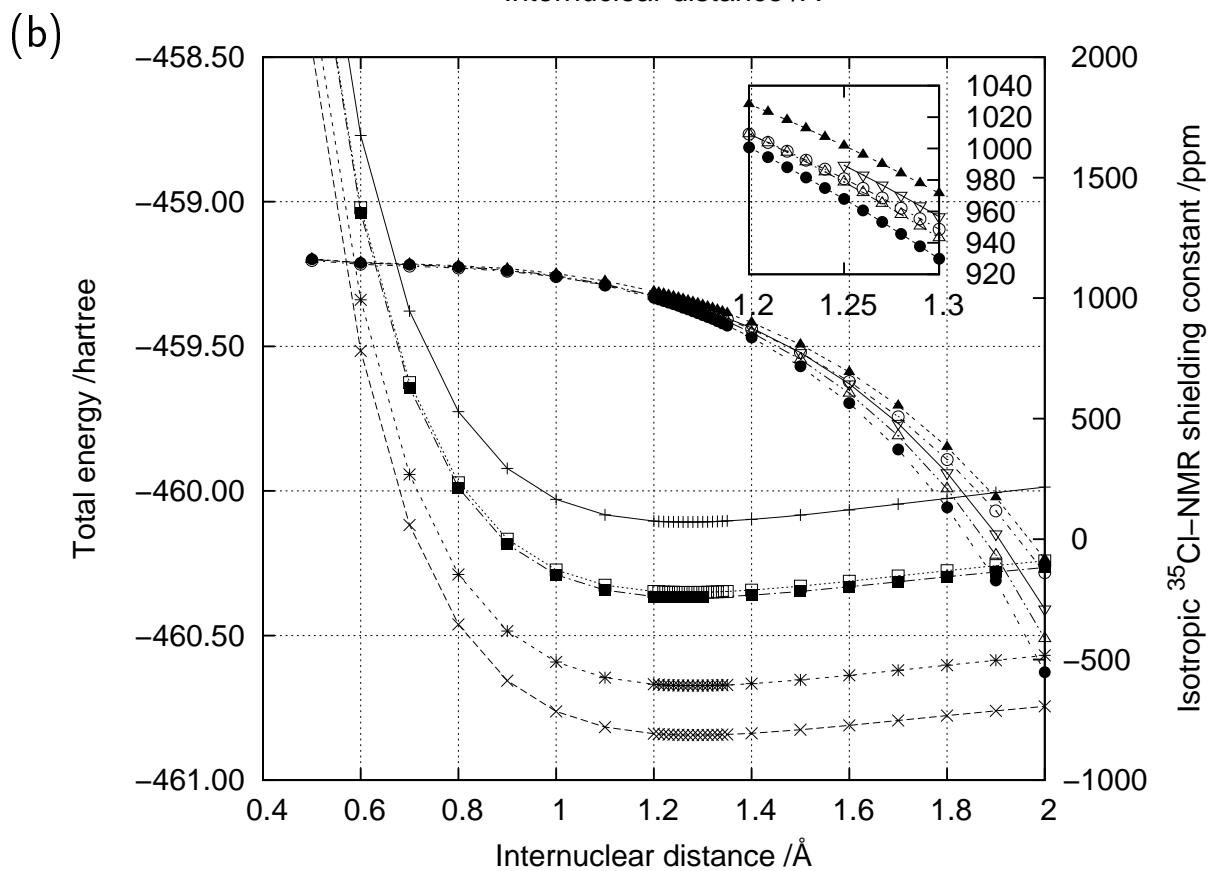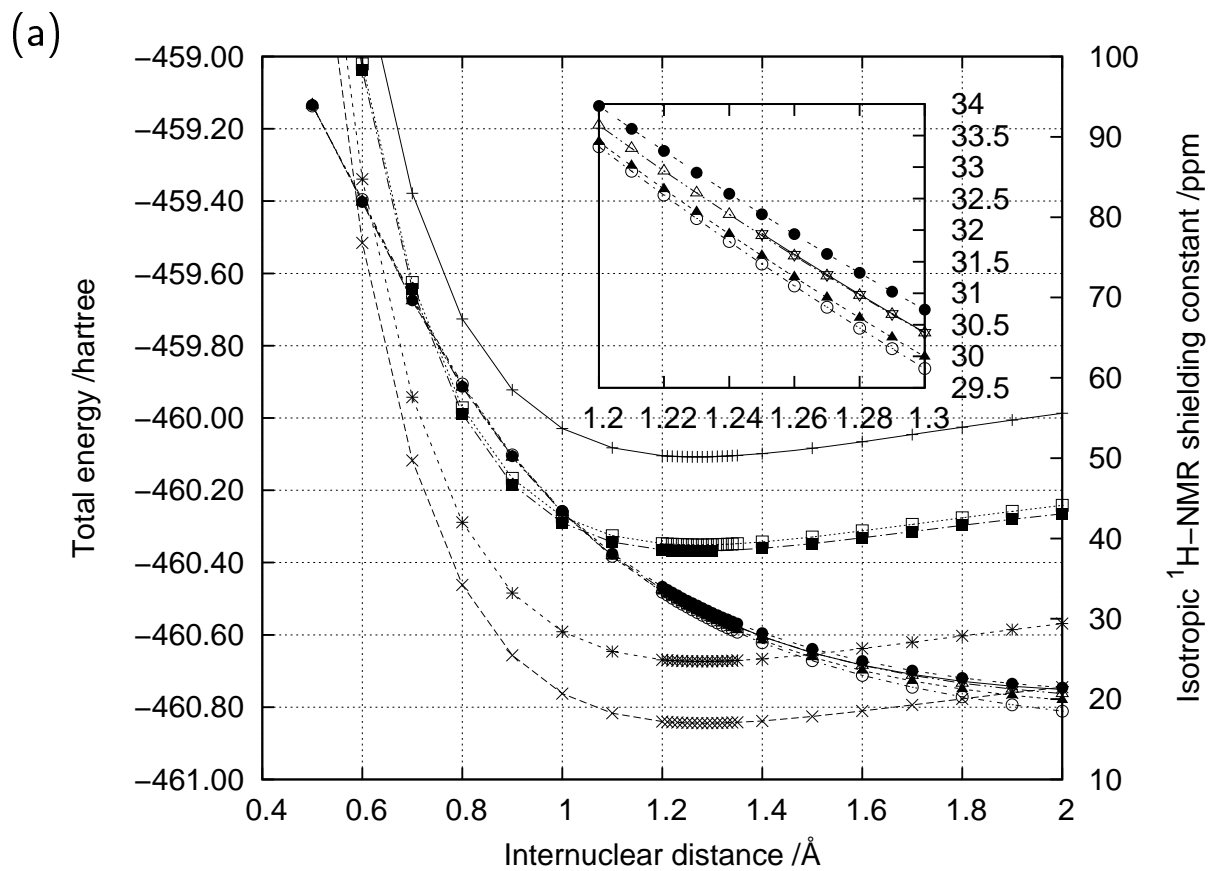
Figure 2 K. Sugimori et al.

(a)

(b)

Figure 3 K. Sugimori et al.