March 2008 Chem. Pharm. Bull. **56**(3) 323—327 (2008)

Properties of the Solute–Stationary Liquid Interactions in Gas Liquid Chromatography

Hideko KAWAKI

Pharmaceutical Research and Technology Institute, Kinki University; 3–4–1 Kowakae, Higashi-Osaka 577–8502, Japan.
Received November 12, 2007; accepted December 14, 2007; published online December 18, 2007

The solute–stationary liquid interaction in gas liquid chromatography (GLC) was determined using Eyring's model. The interaction was determined to be the physical adsorption. The descriptor σ_M was derived and estimated by van der Waals interactions. The CH/π interaction energies were calculated by Tsuzuki *et al.* using the high-level *ab initio* calculations. The CH/π interaction energy was concluded to consist of the dispersion energy (E_{dis}) rather than the electrostatic (E_{es}) and charge-transfer (E_{ct}) energies. These energies were in good agreement with our descriptor σ_M. Furthermore, the macroscopic σ_M also had microscopic support through the weak CH/π interactions. In substituted benzenes, regression analyses were carried out using σ_M for the relative retention values, log γ, as a measure of the solute–stationary liquid interaction. The analyses revealed good results under non-polar conditions. The log γ values therefore consisted primarily of contributions from the dispersion interaction and the CH/π complex. Moreover, these values were useful when added to the electrostatic term (our descriptor σ_{es}) for polar solutes. That is, the log γ values were estimated by the regression analyses using both σ_M and σ_{es}, and were in good agreement with the predicted values.

Key words physical adsorption; van der Waals interaction; CH/π interaction; gas liquid chromatography; solute–stationary liquid interaction; substituted benzene

Noncovalent interactions are very important in molecular recognition of biochemistry, molecular crystals,[1—3] and host-guest complexes.[4] In addition, they play a key role in determining the molecular orientation in molecular assemblies. The weak interaction between the C–H bond and the aromatic π system called the CH/π interaction,[5] has been determined to be a primary contributor to the electrostatic and charge-transfer terms[5,6] based on primary *ab initio* calculations using a small basis set. In recent years, high-level *ab initio* calculations of the typical CH/π complex have shown that dispersion is a major source of attraction.[7—9] MP2 interaction energy depends strongly on the basis set and small basis sets (6-31G*, 6-311G** and cc-pVDZ) greatly underestimate the attraction. Therefore, MP2/cc-pVXZ (X=T or Q) or MP2/aug-cc-pVXZ (X=D or T) level calculations are necessary for quantitative evaluation of the dispersion energy.[10] The estimated CCSD(T) interaction energy for a methane–benzene complex as an example of a typical CH/π interaction at the basis set limit (D_e) was reported to be $-1.43\,\text{kcal mol}^{-1}$ by Shibasaki *et al.*[10] Takahashi *et al.*[11] reported a value of $-1.01\,\text{kcal mol}^{-1}$ for the same structure using MP2/6-311++G (d, p) level calculations. The binding energy D_o was estimated by the D_e and vibrational zero-point energy. This value showed that the former D_o ($1.13\,\text{kcal mol}^{-1}$) was close to the experimental D_o (1.03—$1.13\,\text{kcal mol}^{-1}$). Furthermore, DEF calculations were discussed using BLYP, B3LYP, PW91 and PBE functions were determined to be in appropriate for the quantitative evaluation of the CH/π interaction energy.[12—14] The calculated energy $E_{\text{CCSD(T)(limit)}}$ was determined to be appropriate for a quantitative evaluation of the CH/π interaction.

In the solute–staitonary liquid interaction of gas liquid chromatography, the entropy changes $\Delta\Delta S_s^o$ of dissolution were determined to be correlated to the descriptor σ_M in order to evaluate a physical adsorption using Eyring's model.[15,16] These findings supported the fact that van der Waals interactions were responsible for the formation CH/π complexes between C–H bond of squalane as the stationary liquid and the aromatic π system of the solute. Herein, we discuss the physical origin of the microscopic conditions under which the descriptor σ_M is correlated to the CH/π interaction energy introduced into the high-level *ab initio* calculations.

Experimental

Relative Retention Value log γ The log γ defined by Eq. 1.[17]

$$\log\gamma=\log[t_R(B)/t_R(A)]=-[\Delta H_s^\circ(B)-\Delta H_s^\circ(A)]/2.303RT \\ +[\Delta S_s^\circ(B)-\Delta S_s^\circ(A)]/2.303R \qquad (1)$$

Where $t_R(A)$ and $t_R(B)$ are the retention times of the reference and substituted benzenes, respectively. ΔH_s^o and ΔS_s^o denote the enthalpy and entropy of dissolution of A and B. All data for log γ and the thermodynamic parameters were cited in references,[18—20] and the regression analyses were carried out using the statistical program.[21]

Descriptors σ_M and σ_{es} for Regression Analysis The descriptor σ_M was derived from the Eyring's method: The activated translational entropy change $\Delta\Delta S^\dagger_{ABC}$ for Eyring's equation[15] is given by the following equation, when there is the interaction between the solutes (A and B are the reference and its derivatives) and the non-polar stationary liquid (where *C* is constant).

$$\Delta S^\dagger_{AC}=-R\ln[(2\pi m_A kTe)^{3/2}/h^3] \qquad (2)$$

$$\Delta S^\dagger_{BC}=-R\ln[(2\pi m_B kTe)^{3/2}/h^3] \qquad (3)$$

Where *R*, *k*, *T* and *h* are the gas constant, Boltzmann's constant, absolute temperature and Plank's constant, respectively.

$$\Delta\Delta S^\dagger_{ABC}=\Delta S^\dagger_{BC}-\Delta S^\dagger_{AC}=-3/2R\ln[2\pi m_B kTe/2\pi m_A kTe] \qquad (4)$$

When *T* is constant, Eq. 5 is given by,

$$\Delta\Delta S^\dagger_{ABC}=-3/2R\ln(m_B/m_A) \qquad (5)$$

where m_A and m_B take the relative molecular mass (M_A and M_B) and $\Delta\Delta S^\dagger_{ABC}$ becomes the linear relation $\ln(M_B/M_A)$. The $\ln(M_B/M_A)$ can now be replaced with the descriptor σ_M as follows,

$$\ln(M_B/M_A)=2.303\log(M_B/M_A)=\sigma_M \qquad (6)$$

$$\Delta\Delta S^\dagger_{ABC}\propto\sigma_M \qquad (7)$$

The descriptor σ_M is evaluates the van der Waals interaction energy as phys-

e-mail: kawaki@msa.kindai.ac.jp

ical adsorption.

The descriptor σ_{es} can be derived from induction and orientation energies: Induction energy is defined by the following equations:

$$E_{\text{ind, AC}}=-[(\alpha_A\mu_C^2+\alpha_C\mu_A^2)]/r_{AC}^6 \qquad (8)$$

$$E_{\text{ind, BC}}=-[(\alpha_B\mu_C^2+\alpha_C\mu_B^2)]/r_{BC}^6 \qquad (9)$$

α and μ are polarizability[22] and dipole moment,[23] respectively. When r_{AC}^6 and r_{BC}^6 equal $\alpha_A\alpha_C$ and $\alpha_B\alpha_C$, and μ_C^2/α_C is the constant, both $E_{\text{ind, AC}}$ and $E_{\text{ind, BC}}$ are correlated to $\mu^2{}_A/\alpha_A$ and $\mu^2{}_B/\alpha_B$, respectively.

The descriptor σ_{es} is defined by the following equation,

$$\sigma_{es}=\log[(\mu_B^2/\alpha_B)/(\mu_A^2/\alpha_A)] \qquad (10)$$

The μ_A of benzene reference is 0.31 D[24,25] for $\mu_{\text{Csp3-H}}$.

$\Delta E_{\text{ind, ABC}}$ is related to σ_{es} and the orientation energy change $\Delta E_{\text{ori, ABC}}$ is defined by,

$$\Delta E_{\text{ind, ABC}} \propto \sigma_{es} \qquad (11)$$

$$\Delta E_{\text{ori, ABC}} \propto \sigma_{es} \qquad (12)$$

The descriptor σ_{es} can be evaluated by both induction and orientation energies, and is identical to the electrostatic interaction energy.

Results and Disscussion

Relation between Interaction Energy of Substituted Methane–Benzene and Methane-Substituted Benzene Complexes and the Descriptor σ_M The electrostatic and charge-transfer terms have been reported to be very important based on the primary calculations of CH/π complexes.[5,6] However, typical CH/π complexes such as benzene–methane[7—9] have been shown primarily of dispersion interactions based on high-level *ab initio* calculations. The interaction energies were also consistent with the experimental binding energy D_0 of benzene–X (X=methane,[10] ethylene and acetylene,[26] and benzene[27,28]) as CH/π complexes and benzene–XH$_2$ (X=N[29] and O[30—32]) as the T-shape form of hydrogen bonds. Both the calculated and experimental binding energies in the weak interaction showed a linear correlation, as shown in Fig. 1.

Therefore, the high-level *ab initio* calculation is suitable for the evaluation of the CH/π interaction energy as the dispersion interaction is the major source of the attraction. Results of the calculation suggested that σ_M values were good linear relations to the total energy E_{total} of the typical complexes such as methane–benzene[33] and activated complexes such as halomethane–benzene[8,34] as shown in Fig. 2. The interaction between the acidic CH group and π-electrons in the halomethane–benzene complex was categorized as a conventional π–hydrogen bond rather than as a van der Waals interaction.[35] The large slope observed in Fig. 2 represents the halomethane–benzene series, and the difference between the two slopes accounts for the electrostatic interaction.

The regression analyses of E_{total} are given by,

$$-E_{total}=5.16(0.51)\sigma_M-2.51(0.47) \qquad (13)$$

n=14, r=0.946, F=102.0, S.D.=0.17

(CH_4–C_6H_6, –C_6H_5Me, –$C_6H_4Me_2$, –$C_6H_3Me_3$, –$C_{10}H_8$, C_6H_6–C_2H_6, –CH_3NH_2, –CH_3OH, –CH_3OCH_3, –C_6H_6, –$C_6H_5CH_3$, –C_6H_5OH, –C_6H_5F, –C_6H_5CN)

$$-E_{total}=12.20(0.94)\sigma_M-7.81(0.86) \qquad (14)$$

n=12, r=0.972, F=169.2, S.D.=0.29

(C_6H_6–CH_4, C_6H_6–C_2H_4, –C_2H_2, –CH_3F, –CH_3Cl, –CH_2ClNH_2, –CH_2ClOH, –CH_2Cl_2, –CH_2FCl, –CH_2F_2, –$CHCl_3$, –CHF_3)

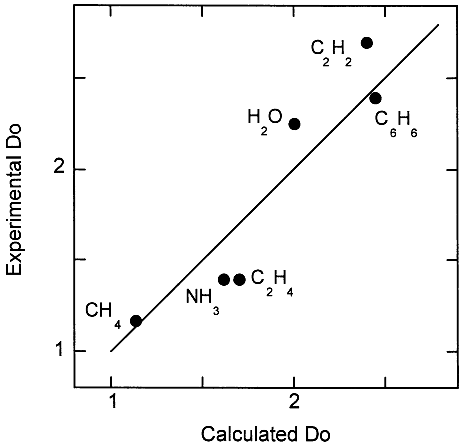

Fig. 1. Correlation between the Calculated and Experimental Binding Energies D_0/kcal mol^{-1} with Benzene Complexes

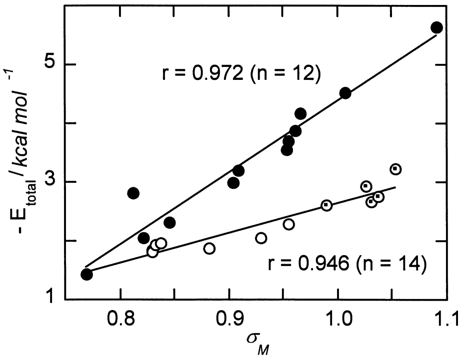

Fig. 2. Plots of CH/π Interaction Energy E_{total} *versus* the Descriptor σ_M

○, ● and ◎ estimated E_{total} by Tsuzuki *et al.* and Morita *et al.*, and by Sinnokrot *et al.*,[38] respectively.

$$-E_{total}=6.82(0.53)\sigma_M-0.82(0.06)E_{es}-4.11(0.49) \qquad (15)$$

n=25, r=0.976, F=225.5, S.D.=0.23

These findings suggest that the typical and activated CH/π complexes consisted primarily of the dispersion energy E_{dis} (Eqs. 13, 14). The difference of two groups is E_{es} and it is negligible small for the typical CH/π complex. The two groups (Eqs.13, 14) could be defined by one equation as in Eq. 15, since E_{es} contributed to the activated CH/π complex. The typical CH/π complex differs from the hydrogen bond and the orientation dependence is very small. On the other hand, the activated CH/π complex is close to weak hydrogen bond as C_6H_6–H_2O *etc.*[36] The descriptors σ_M will be compared with the correlation interaction energy E_{corr} in the following section.

The Relationship between E_{corr} and σ_M The relationship between E_{corr} and σ_M was linear up to relative large energy values in the activated CH/π interaction. The relationship could be described by the following regression analyses, as shown in Fig. 3.

$$E_{corr}=-17.03(1.92)\sigma_M+11.45(1.78) \qquad (16)$$

n=9 (C_6H_6–CH_3F, –CH_3Cl, –CH_2ClNH_2, CH_2ClOH, –CH_2Cl_2, –CH_2FCl, –$CHCl_3$, –C_2H_2, –CH_4), r=0.958, F=78.9, S.D.=0.54

The σ_M is proposed to be representative of the E_{dis}, since the E_{corr} consists primarily of attractive dispersion energy.

The Relationship between E_{es} and σ_{es} Hartree–Fock

(HF) calculation does not depend on the basis set. Therefore, the descriptor σ_{es} values were comparable with the electrostatic energies E_{es} using MP2/6-31G*(0.25) in pyridine-substituted benzenes complexes[37)] (Fig. 4).

This regression analyses is given by,

$$\Delta E_{es} = -0.23(0.04)\sigma_{es} - 0.08(0.06) \qquad (17)$$

$n=8$ (H, Me, OH, NH_2, CHO, COOH, CN, NO_2), $r=0.905$, $F=27.0$, S.D.$=0.09$

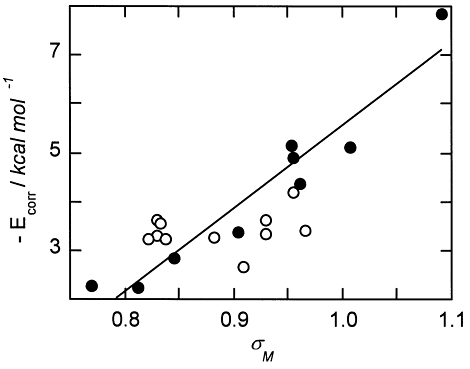

Fig. 3. Correlation between E_{corr} and the Descriptor σ_M in Benzene–Methanes and Methane–Benzenes Complexes

● and ○ are chloro- and substituted compounds, respectively.

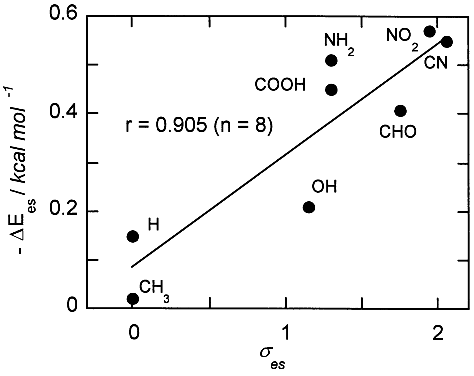

Fig. 4. Correlation between $-\Delta E_{es}$ of Pyridine–Monosubstituted Benzenes Complexes and the Descriptor σ_{es}

The two descriptors σ_M and σ_{es} were in good agreement with E_{corr} and E_{es} in Eqs. 16 and 17, respectively. Therefore, both descriptors could be used to estimate the relatively weak interaction. Next, regression analyses were carried out using σ_M and σ_{es} in the solute–stationary liquid interaction.

The Relation between σ_M and $\Delta\Delta S_s^\circ$ The activated translational entropy change $\Delta\Delta S^\dagger$ derived using Eyring's model could be correlated with σ_M. Furthermore, these thermodynamic parameters were obtained, because the relative retention values, $\log\gamma$, varied with temperature. If the interactions were based on physical adsorption, the resolution entropy changes $\Delta\Delta S_s^\circ$ would be related to σ_M. The $\Delta\Delta S_s^\circ$ (np) values showed a linear relationship for mono-substituted benzenes–squalane under non-polar conditions. (Fig. 5).

These results suggested that the solute–stationary liquid interaction primarily consisted of van der Waals interactions, which was reflected in the physical adsorption. Table 1 shows a list of regression analyses for mono-, 1,3- and 1,4-substituted benzenes under non-polar conditions. The predicted values were fitted to the observed values (Fig. 6).

The $\Delta\Delta S_s^\circ$ (sp) values estimated under semi-polar conditions as (dinonyl phthalate) were also analyzed using σ_M. Furthermore, the values were well fit in addition to descriptor σ_{es}. When the stationary phase was polar, the contribution from σ_{es} was significant. The solute–stationary liquid inter-

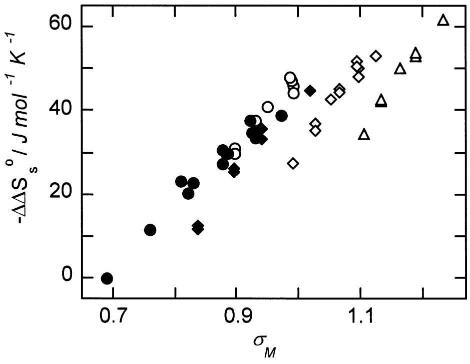

Fig. 5. Correlation between the Entropy Change $\Delta\Delta S_s^\circ$ and the Descriptor σ_M in Substituted Benzenes

●=R, H; ◆=F, R; ○=Cl, R; ◇=Br, R; △=I, R compounds.

Table 1. The Results of the Regression Analyses for the Resolution Entropy Changes $\Delta\Delta S_s^\circ$ and Relative Retention Values, $\log\gamma$, in for the Solute–Squalane Interactions for Substituted Benzenes

	Coeff. of σ_M	Coeff. of σ_{es}	Const.	$n^{a)}$	$r^{b)}$	$F^{c)}$	S.D.$^{d)}$
$-\Delta\Delta S_s^\circ$	206.64 (11.57)		2.41 (1.51)	13	0.982	296.6	2.16
$-\Delta\Delta S_s^\circ$	190.64 (15.18)		−145.95 (13.88)	8	0.982	157.8	2.41
$-\Delta\Delta S_s^\circ$	165.61 (15.05)		−117.18 (14.35)	9	0.972	121.2	1.65
$-\Delta\Delta S_s^\circ$	195.25 (13.74)		−164.56 (14.71)	12	0.976	201.9	1.76
$-\Delta\Delta S_s^\circ$	206.64 (11.57)		−192.28 (13.47)	7	0.992	318.9	1.25
$-\Delta\Delta S_s^\circ$	143.56 (5.93)		−98.54 (5.61)	49	0.962	585.8	3.49
$\log\gamma$	4.308 (0.334)		−2.936 (0.288)	13	0.968	165.9	0.089
	3.934 (0.246)	0.087 (0.023)	−2.696 (0.204)		0.987	190.68	0.060
$\log\gamma$	4.247 (0.226)		−2.935 (0.213)	18	0.978	353.7	0.085
	3.842 (0.226)	0.087 (0.028)	−2.661 (0.194)		0.987	274.2	0.068
$\log\gamma$	4.626 (0.254)		−3.199 (0.243)	13	0.984	332.9	0.093
	4.196 (0.217)	0.108 (0.031)	−2.953 (0.185)		0.993	342.4	0.066
$\log\gamma$	4.942 (0.331)		−3.462 (0.317)	24	0.954	222.5	0.143
	3.959 (0.279)	0.179 (0.032)	−2.775 (0.241)		0.982	277.9	0.091
$\log\gamma$	4.653 (0.188)		−3.236 (0.178)	64	0.953	614.8	0.123
	4.099 (0.165)	0.126 (0.019)	−2.886 (0.145)		0.973	549.9	0.094

a,b,c,d) The number of data, correlation coefficient, variance ratio and standard deviation, respectively.

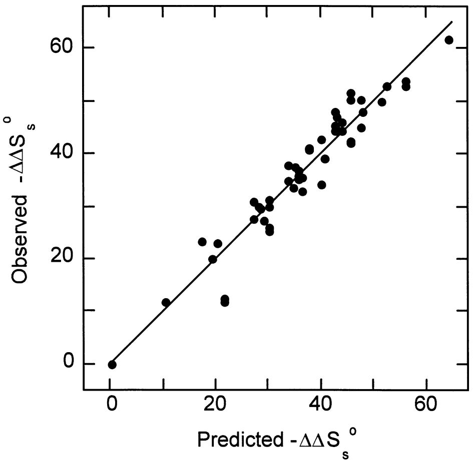

Fig. 6. Correlation between the Predicted and Observed Entropy Changes $\Delta\Delta S_s^\circ/J\,\text{mol}^{-1}\,\text{K}^{-1}$ in Substituted Benzene–Squalane Complexes

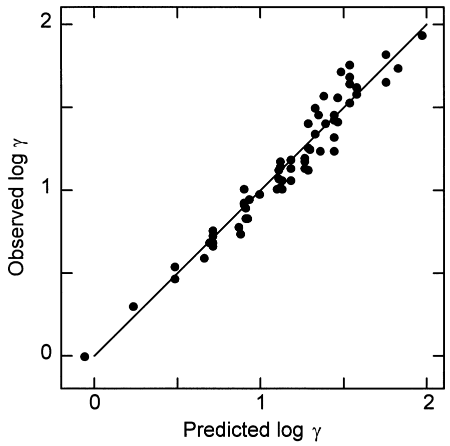

Fig. 7. Correlation between the Predicted and Observed log γ in Substituted Benzene–Squalane Complexes

action however consisted with primarily van der Waals interactions. Further the standard coefficients for σ_M were greater than 98% and 80% under non- and semi-polar conditions, respectively, in GLC.

$$-\Delta\Delta S_s^\circ(\text{np})=131.79(7.44)\sigma_M+1.62(0.69)\sigma_{es}+2.01(1.28) \quad (18)$$

$n=13$ (H, Me, Et, n-Pr, n-Bu, OMe, OEt, COMe, COEt, CO_2Me, CO_2Et, CN, NO_2), $r=0.988$, $F=211.0$, S.D.$=1.82$

$$-\Delta\Delta S_s^\circ(\text{sp})=147.67(9.39)\sigma_M+6.71(0.88)\sigma_{es}+3.35(1.61) \quad (19)$$

$n=13$, $r=0.990$, $F=241.5$, S.D.$=2.30$

Regression Analyses of the Relative Retention Value log γ The relative retention values log γ were analyzed using two descriptors σ_M and σ_{es} for mono- and di-substituted benzenes–squalane interactions under non-polar conditions (Table 1).

The observed values for log γ were in good agreement with predicted values (Fig. 7). Therefore, the descriptor σ_M is expected to be useful for determining the relative contribution of very weak interactions such as the CH/π interaction.

Conclusion

The solute–stationary liquid interaction in GLC was determined using Eyring's model to be the physical adsorption. The descriptor σ_M derived using Eyring's model was used to estimate the van der Waals interactions and was in good agreement with the CH/π interaction energy introduced into high-level *ab initio* calculations. This suggested that the solute–stationary liquid interaction for halo-benzenes consisted primarily of van der Waals interactions under the gas conditions. In other words, the induced macroscopic σ_M was correlated with the microscopic high-level calculated energy as the CH/π interaction. Regression analyses of the log γ values were carried out using σ_M and the predicted values were determined to be in good agreement with the observed values.

References and Notes

1) Karle I. L., Butcher R. J., Wolak M. A., Silva F., Dementrio A., Uchida M., Breads J.-L., Kafafi Z. H., *J. Phys. Chem., C*, **111**, 9543—9547 (2007).
2) Sada K., Miyata M., Matsumoto A., *Cryst. Growth Des.*, **3**, 247—256 (2003).
3) Matsumoto A., Tanaka T., Tsubouchi T., Tashiro K., Saragai S., Nakamoto S., *J. Am. Chem. Soc.*, **124**, 889—902 (2002).
4) Umezawa Y., Nishio M., *Bioorg. Med. Chem.*, **6**, 493—504 (1998).
5) Nishio M., Hirota M., Umezawa Y., "The CH/π interaction," Wiley-VCH, New York, 1998.
6) Sakaki S., Kato K., Miyazaki T., Musashi Y., Ohkubo K., Ihara H., Hirayama C., *J. Chem. Soc. Faraday Trans.*, **89**, 659—664 (1993).
7) Tarakeshwar P., Choi H. S., Kim K. S., *J. Am. Chem. Soc.*, **123**, 3323—3331 (2001).
8) Tsuzuki S., Honda K., Uchimaru T., Mikami M., Tanabe K., *J. Phys. Chem., A*, **106**, 4423—4428 (2002).
9) Sundararajan K., Sankaran K., Viswandthan K. S., Kulkarni A. D., Gadre S. R., *J. Phys. Chem., A*, **106**, 1504—1510 (2002).
10) Shibasaki K., Fujii A., Mikami N., Tsuzuki S., *J. Phys. Chem., A*, **110**, 4397—4404 (2006).
11) Takahashi O., Kohno Y., Iwasaki S., Saito K., Iwaoka M., Tomoda S., Umezawa Y., Tsuboyama S., Nishio M., *Bull. Chem. Soc. Jpn.*, **74**, 2421—2430 (2001).
12) Meijer E. J., Sprik M., *J. Chem. Phys.*, **105**, 8684—8689 (1996).
13) Tsuzuki S., Luthi H. P., *J. Chem. Phys.*, **114**, 3949—3957 (2001).
14) Sato T., Tsuneda T., Hirao K., *Mol. Phys.*, **103**, 1164—1151 (2005).
15) Glasstone S., Laidler K. J., Eyring H., "The Theory of Rate Processes—The Kinetics of Chemical Reactions, Viscosity, Diffusion and Electrochemical Phenomena—," Chapter VII, McGraw-Hill, Inc., New York, 1941.
16) Kawaki H., *Chem. Pharm. Bull.*, **52**, 221—225 (2004).
17) Littlewood A. B., Phillips C. S. G., Price D. T., *J. Chem. Soc.*, **1955**, 1480—1489 (1955).
18) Kawaki H., *Chem. Pharm. Bull.*, **41**, 797—803 (1993).
19) Kawaki H., *Chem. Pharm. Bull.*, **49**, 5—9 (2001).
20) Kawaki H., Sasaki Y., Takagi T., Fujii S., Masuda F., *Chem. Pharm. Bull.*, **37**, 3268—3271 (1989).
21) Aoki S., ⟨htto://aoki2.si.gumma-u.ac.jp/BlackBox⟩.
22) West R. C., "Handbook of Chemistry and Physics," 70th, ed. by CRC Press. Inc., Boca Raton, Florida, 1989—1990, pp. C4—C551.
23) McClellan A. L., "Tables of Experimental Dipole Moments," Freeman, San Francisco, 1963.
24) Rollefson R., Havens R., *Phys. Rev.*, **57**, 710—717 (1940).
25) Petro A., *J. Am. Chem. Soc.*, **80**, 4230—4232 (1958).
26) Shibasaki K., Fujii A., Mikami N., Tsuzuki S., *J. Phys. Chem., A*, **111**, 753—758 (2007).
27) Grover J. R., Walters E. A., Hui E. T., *J. Phys. Chem.*, **91**, 3233—3237 (1987).
28) Lee E. C., Kim D., Jurecka D., Tarakeshwar P., Hobza P., Kim K. S., *J. Phys. Chem., A*, **111**, 3446—3457 (2007).
29) Rodham D. A., Suzuki S., Suenram R. D., Lovas F. J., Dasgupta S., Goddard III, W. A., Blake G. A., *Nature* (London), **362**, 735—737 (1993).
30) Gotch A. J., Zwier T. S., *J. Chem. Phys.*, **96**, 3388—3401 (1992).
31) Cheng B.-M., Grover J. R., Walters E. A., *Chem. Phys. Lett.*, **232**, 364—369 (1995).
32) Courty A., Mons M., Diminicoli I., Piuzzi F., Dimmicoli I., *J. Phys.*

Chem., *A*, **101**, 1445—1450 (1997).

33) Morita S., Fujii A., Mikami N., Tsuzuki S., *J. Phys. Chem.*, *A*, **110**, 10583—10590 (2006).

34) Tsuzuki S., Honda K., Uchimaru T., Mikami N., Fujii A., *J. Phys. Chem.*, *A*, **110**, 10163—10168 (2006).

35) Fujii A., Morita S., Miyazaki M., Ebata T., Mikami N., *J. Phys. Chem.*, *A*, **108**, 2652—2658 (2004).

36) Tsuzuki S., Honda K., Uchimaru T., Mikami M., Tanabe K., *J. Am. Chem. Soc.*, **122**, 11450—11458 (2000).

37) Mignon P., Loverix S., DeProft F., Geerling P., *J. Phys. Chem.*, *A*, **108**, 6038—6044 (2004).

38) Sinnokrot M. O., Sherrill C. D., *J. Am. Chem. Soc.*, **126**, 7690—7697 (2004).