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Effective Interaction Energies for Weakly Bound Dimers at Room Temperature: $(H_2O)_2$, $(N_2O)_2$, $(CO_2)_2$, and $(HCHO)_2$

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Effective dimer bond energies at room temperature are experimentally determined by pressure broadening for rotational lines. Toward the understanding of the bond energies, thermal energies associated to the dissociation are theoretically evaluated by considering effective degrees of freedom.

Previously, we have reported the effective interaction energy at room temperature for water dimer based on the pressure broadening of the rotational lines. The result was compared with ab initio molecular orbital (MO) Monte Carlo (MC) simulation, showing a good agreement.[1] The agreement is due to the fact that the experimental observation is directly related to the nature of the interaction energy in collisional processes. Experimentally obtained interaction energies for several dimers were reported by applying an energy-transfer model to observed pressure broadening coefficients for rotational spectra.[2,3] As for bond dissociation energies of dimers, minimum energy at the optimized configuration is often considered using standard ab initio MO computations, which corresponds to the frozen structure at 0 K. MC simulation takes into account a finite temperature effect, but dynamic aspects corresponding to the collision cannot be considered. Experimentally obtained interaction energies enter essentially as the heat of the reaction for complex formation,[4] including the effective thermal energy at 298 K. Thus, the essential motion related to the dimer bond dissociation has to be extracted, and its energy, which may represents the effective thermal energy, has to be estimated. Namely, thermodynamic quantities such as free energy may not be inadequate to explain the experimental observation related to a short-time dynamic event. In the present work, a simple model to evaluate the effective interaction energy is proposed using the potential energy well depth (D_e) and vibrational frequencies for H_2O, CO_2, N_2O, and HCHO dimers. We extracted vibrational thermal energies associated to dissociation of dimers by considering effective degrees of freedoms along the dissociation in each normal mode. Finally, presently calculated values are compared with reported experimental values that were obtained by the pressure broadening method for rotational lines.

When a non-colinear monomer molecule consists of N atoms, the dimer has $(6N - 6)$ degrees of vibrational freedom. $(6N - 12)$ modes are attributed to the intramolecular stretching in monomers. The remaining 6 modes are assigned to twist-type motions as well as to the collisional motion. In a similar manner, 4 modes are related to the intermolecular motion for the linear monomer system. To elucidate essential motions in the dissociation, the following procedure has been employed: the motion of the monomer complex is characterized by the normal modes (Q_i), while the direction of dissociation can be defined by a normalized vector in three-dimensional space ($\mathbf{e}_g$) parallel to the direction between the centers of mass of two monomers. For example, in the case of a four-atomic system (two diatomic-molecule system), Q_i is expressed as a column vector in twelve-dimensional space and given by a standard normal mode analysis of ab initio MO computations. Projection of Q_i on $\mathbf{e}_g$ indicates how strongly the mode is correlated to the dissociative motion; namely, the weight of dissociation in Q_i is given by

$$\theta_i = \left| \frac{1}{\sqrt{4}} (\mathbf{e}_g{}^T, \mathbf{e}_g{}^T, -\mathbf{e}_g{}^T, -\mathbf{e}_g{}^T) Q_i \right| \tag{1}$$

where T means transpose of vector. Note that signs of elements ($\mathbf{e}_g$) are different for each monomer. If Q_i coincides with the dissociative motion perfectly, the quantity θ_i equals unity. For Q_i representing a torsional mode, θ_i is expected to become zero. A diagram for a dimer of diatomic molecules is schematically shown in Figure 1. The effective thermal energy $\langle \varepsilon^V \rangle$ for intermolecular stretching modes of a dimer at temperature, T, may be evaluated from vibrational partition functions with harmonic approximation.

$$\langle \varepsilon^V \rangle = \sum_i \theta_i \frac{hc\tilde{\nu}_i}{e^{hc\tilde{\nu}_i/k_B T} - 1} \tag{2}$$

where $\tilde{\nu}$ is the wavenumber, h is Plank's constant, and c is the velocity of light. Equation 2 is derived from the temperature-dependent part of the partition function for intermolecular vibrational motions, $z = \prod_i z_i^{\theta_i}$, meaning that essential motions are extracted by considering effective degrees of freedoms (θ_i) along the dissociation in each normal mode. Remaining degrees of freedoms $(1 - \theta_i)$ are assigned to other motions such as torsional motion, which are much less significant for the thermal correction on the dissociation. It is also noted that the present

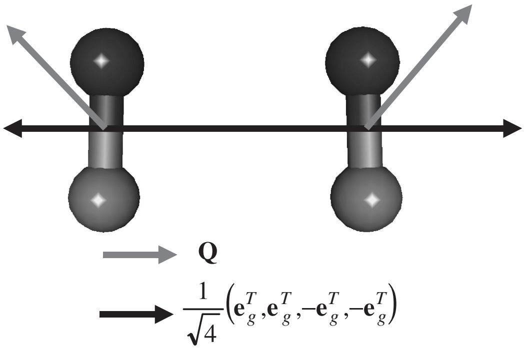

Figure 1. A diagram for effective degrees of freedoms (θ) along the dissociation in the case of a dimer of diatomic molecules. The black line represents a normalized vector parallel to the direction between the centers of mass of two monomers. The gray line (***Q***) is a normal mode of dimer.

Table 1. Calculated and experimental energies for dimers (in units of $kJ\,mol^{-1}$)

	Molecule			
	$(H_2O)_2$	$(CO_2)_2$	$(N_2O)_2$	$(HCHO)_2$
Potential well depth (D_e)	22.1	6.74	8.16	20.0
Zero-point energy (ZPE)	9.0	1.21	0.71	6.99
Dimerization energy (D_0)	13.1	5.52	7.45	13.0
Thermal energy ($\langle \varepsilon^V \rangle$)[a]	1.59	2.85	3.05	2.59
$D_0 - \langle \varepsilon^V \rangle$	11.5	2.68	4.39	10.4
Experimental value	13.4	3.8	5.0	9.4
at room temperature[b]	(4.2)	(0.4)	(0.8)	(0.14)
Reference	1	2	2	3

[a] Equation 2 for thermal energies of vibrational modes related to dissociation for dimers at 298 K. [b] Measured with pressure broadening technique. Error bars are in parentheses.

method of correction differs from both a standard thermodynamic treatment and the energetics of static (nondynamical) molecular systems.

Table 1 shows our computational results for the potential well depth (D_e) with optimized structures for dimers, which were evaluated with the MP2/aug-cc-pVTZ level of computations using g03.[5] Monomers and dimers were respectively optimized. The interaction energy at $T = 0\,K$ is given by $D_0 = D_e - ZPE$ with use of the calculated vibrational frequencies. Some of the optimized geometries of dimers are listed in Table SI of the Supporting Information.[6] The calculated intermolecular frequencies and θ are also listed in Table SII.[6] Using them, the effective vibrational thermal energies, $\langle \varepsilon^V \rangle$, and the effective interaction energies at 298 K, $D_0 - \langle \varepsilon^V \rangle$, are calculated as listed in Table 1. Note that the number of presently considered modes is six for H_2O and HCHO dimers and four for the dimers of collinear CO_2 and N_2O.

For H_2O dimer, by subtracting the thermal energy of $1.59\,kJ\,mol^{-1}$ from D_0, the present estimated effective interaction energy is $11.5\ (= 13.1 - 1.59)\,kJ\,mol^{-1}$. Huang et al. made a precise calculation of D_0, using a very accurate potential energy surface in full dimensionality based on CCSD(T)/AVTZ energies and Diffusion MC calculation of the dimer zero-point energy.[7,8] If Huang's values are adopted, it would be $10.8 \sim 11.9$ $[= (12.4 \sim 13.5) - 1.59]\,kJ\,mol^{-1}$. In our previous report, the effective interaction energy at room temperature was estimated by ab initio MC simulation for various configurations of the dimer to be $13.9\,kJ\,mol^{-1}$.[1] These theoretical values are in good agreement with the value obtained from pressure broadening measurements at room temperature, $13.4 \pm 4.2\,kJ\,mol^{-1}$.[1] It should be noted that the present potential energy surface and its minimum are different from our previous ab initio MC simulation because a larger basis set is employed in the present study.

For N_2O and CO_2 dimers, the present theoretically estimated effective interaction energies are $4.39\,kJ\,mol^{-1}$ for N_2O and $2.68\,kJ\,mol^{-1}$ for CO_2, which show fair agreement with effective interaction energies at room temperature obtained from pressure broadening experiments, $5.0 \pm 0.8\,kJ\,mol^{-1}$ for N_2O and $3.8 \pm 0.4\,kJ\,mol^{-1}$ for CO_2.[2]

An experimental estimation of interaction energy with the pressure broadening technique was performed for HCHO by Barry et al.[3] They reported that the experimental value is $9.4 \pm 0.14\,kJ\,mol^{-1}$, which is smaller than the theoretical value of $12.05\,kJ\,mol^{-1}$ calculated by Vila et al.[9] Barry et al.[3] mentioned that their experimental value is influenced by the long-range attractive forces operating on the vibrationally excited state, and the calculated value applies only to the ground state of the dimer.[3] Here, we apply the aforementioned procedure to HCHO dimer. Since two isomers (C_s and C_{2h} structures) are known as stable species, the thermal energy was obtained by averaging with Boltzmann factors. When D_0 of the more stable dimer is considered, the resulting effective interaction energy is $10.4\,kJ\,mol^{-1}$ that is in better agreement with the pressure-broadening result, $9.4 \pm 0.14\,kJ\,mol^{-1}$, of Barry et al.[3]

There should be a few sources causing the discrepancy between computational and experimental values due to incompleteness of the computational level. For example, in computation for the dimer optimized geometry, we assume that structures of interacting molecules are perfectly relaxed during the collision process. Only a few configurations of dimers, which correspond to the local energy minimums, were treated and contributions from other possible configurations were not considered. These treatments could cause overestimation of the interaction energy. In addition, quantitative estimation of the averaged *ZPE* contribution attributed to various configurations was not performed. Neglect of the anharmonicity of the potential energy surface may also cause overestimation of the *ZPE*. BSSE could be another source of errors. At the present, we cannot exclude the possibility to cancel out of these error sources. However, in spite of these incompleteness factors, the present simple procedure can provide a reasonable estimation of the effective interaction energy at room temperature.

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