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The SCF and CI Study on Vibrational Structures of Triatomic van der Waals Complexes: He-I_2 and He-Cl_2

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The vibartional energy levels of triatomic van der Waals complexes, *e.g.*, He-I_2 and He-Cl_2, are studied theoretically. Not only because a weak bond exists in these systems but also because the excited states are of interest, very accurate numerical methods are required to determine vibrational structures of the complexes. The self-consistent-field (SCF) and the configuration interaction (CI) methods are employed to study several low lying bound states. Particularly the useful but approximate SCF method is extensively studied by comparing its results with those of in-principle-accurate CI method. It is found that the SCF method produces reasonable vibrational energy levels when Jacobi coordinates are utilized.

Introduction

The van der Waals complexes, *i.e.*, molecules having at least one chemically weak van der Waals bond, have attracted a lot of attention both experimentally and theoretically.[1~22] Experimental techniques such as high-resolution IR absorption spectroscopy, Fourier-transform infrared spectroscopy, and microwave spectroscopy provide a wealth of information on the geometrical and vibrational structures of van der Waals complexes. In many weakly bound molecules the deviation from harmonic behavior is very large even for ground vibrational state. It is to obtain the vibrational energy level structure of the complexes from the given potential energy functions and to interpret the level structure in terms of vibrational dynamics involved. The need for theoretical methods arises from the very rapid progress in experimental van der Waals complex spectroscopy.

To determine vibrational structures of polyatomic molecules, harmonic motions are usually assumed to obtain vibrational frequencies. Or sometimes the derivatives of potential energy functions around the minimum are used to determine fundamental vibrational frequencies. These techniques are useful but can not be applied to vibrationally excited states. For diatoms, the direct numerical integration of the relevant Schrödinger equation suffices to produce all the accurate vibrational levels, but for polyatoms it is not easy to perform direct numerical calculations. While the perturbative approach to solve the Schrödinger equation has been introduced, in the present work we adopt the variational methods, *i.e.*, the self-consistent-field (SCF) approximation and the configuration interaction (CI) method.

The SCF and CI methods are widely used in electronic structure calculations, but the vibrational structure calculations using SCF and CI are not frequently reported. In SCF method,[23] each vibrational mode is described as moving in an effective field, being the average of the full potential over the motions of all the other modes. The each vibrational mode consists of wavefunctions called modal wavefunctions corresponding to orbitals in electronic structure theory. Since each modal wavefunction is associated with a formally separate Hamiltonian, the SCF method clearly involves an assumption of mutual separability of vibrational modes. However, the SCF modes are different from normal modes. While normal modes are assumed to be independent to each other, the SCF modes are independent but the effect of other modes are already incorporated in an average sense. Yet in the SCF method, still "the correlation" between modes is not included. Therefore the validity and accuracy of SCF approximation depend on the coordinates used in calculations, because each modal wavefunction is represented with each variable composing the coordinate system chosen. The correlation part missing in SCF approximation is incorporated in CI method. In CI, the true vibrational wavefunctions are expressed in linear combination of configurations which are products of modal wavefunctions. And the CI matrix is set up and diagonalized to have exact vibrational energies and wavefunctions.

We will discuss the theoretical SCF and CI calculations for the vibrational energy levels of two triatomic van der Waals complexes, *e.g.*, He-I_2 and He-Cl_2. We perform the full 3-dimensional calculations and the 2-dimensional calculations with one vibrational mode frozen. The Jacobi coordinates are used and found to be appropriate for describing the complexes because the I-I or Cl-Cl bond is very strong so that one axis should lie along the bond, which is satisfied in Jacobi coordinates.

In the following section, the SCF method, CI method, and the numerical integration method are explained in detail. The following section describes the computational details including the potential energy functions and the calculational results are provided in the last section.

Theory

We utilize the Jacobi coordinates for triatomic van der Waals complexes, AB···C, where C is a rare gas atom and AB is a covalently bonded diatom. The Hamiltonian for AB···C complex can be written as, in atomic units,

$$H(r,R,\theta)=-\frac{1}{2\mu_1 r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)-\frac{1}{2\mu_2 R^2}\frac{\partial}{\partial R}\left(R^2\frac{\partial}{\partial R}\right)+\frac{j^2}{2\mu_1 r^2}+\frac{l^2}{2\mu_2 R^2}+V(r,R,\theta) \tag{1}$$

where r is the internuclear distance between atom A and atom B, R is the distance between rare atom C and the center of mass of diatom AB, and θ is the angle between bond vectors associated with r and R. $\mu_1=m_Am_B/(m_A+m_B)$ is the reduced mass of atom A and B, and $\mu_2=m_C(m_A+m_B)/(m_A+m_B+m_C)$ is the reduced mass of diatom AB and rare atom C. j and l are the two angular momenta associated with r and R, respectively, and the total angular momentum $J(=j+l)$ is considered to be zero. Thus

$$j^2=l^2=\frac{-1}{\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) \tag{2}$$

and $V(r,R,\theta)$ is the potential energy function. The range of θ is defined from 0 to π and the range of R and r is from 0 to ∞.

The Schrödinger equation is

$$H(r,R,\theta)\ \Phi(r,R,\theta)=E\Phi(r,R,\theta) \tag{3}$$

where E is the vibrational energy and $\Phi(r,R,\theta)$ is the vibrational wavefunction. If we substitute $\Phi(r,R,\theta)$ with $\Psi(r,R,\theta)/rR$, the reduced equation is

$$H(r,R,\theta)\ \Psi(r,R,\theta)=E\ \Psi(r,R,\theta) \tag{4}$$

where $\Psi(r,R,\theta)$ is normalized such that $\iiint[\Psi(r,R,\theta)]^2\sin\theta d\theta dRdr=1$. And the reduced Hamiltonian is

$$H(r,R,\theta)=-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2}-\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2}+\frac{j^2}{2\mu_2 r^2}+\frac{l^2}{2\mu_2 R^2}+V_1(r)+V_2(r,R,\theta). \tag{5}$$

$V_1(r)$ is the potential energy function for diatomic molecule AB, while $V_2(r,R,\theta)$ is the rest part of whole potential for van der Waals complex, *i.e.*, $V(r,R,\theta)=V_1(r)+V_2(r,R,\theta)$.

The self-consisten-field (SCF) wavefunction for (v_1,v_2,v_3) state is a product of modal wavefunctions,[16] *i.e.*,

$$\Psi_{v_1v_2v_3}(r,R,\theta)\approx\Psi^{\mathrm{SCF}}{}_{v_1v_2v_3}(r,R,\theta)=\psi^1{}_{v_1}(r)\psi^2{}_{v_2}(R)\psi^3{}_{v_3}(\theta) \tag{6}$$

$$H^{\mathrm{SCF}}(r,R,\theta)\Psi^{\mathrm{SCF}}_{v_1v_2v_3}(r,R,\theta)=E^{\mathrm{SCF}}_{v_1v_2v_3}(r,R,\theta). \tag{7}$$

Then the modal wavefunctions ψ should satisfy

$$H^{\mathrm{SCF}}(r,R,\theta)=h_1(r)+h_2(R)+h_3(\theta) \tag{8}$$

$$h_1(r)\psi^1{}_{v_1}(r)=\varepsilon^1{}_{v_1}\psi^1{}_{v_1}(r) \tag{9}$$

$$h_2(R)\psi^2{}_{v_2}(R)=\varepsilon^2{}_{v_2}\psi^2{}_{v_2}(R) \tag{10}$$

$$h_3(\theta)\psi^3{}_{v_3}(\theta)=\varepsilon^3{}_{v_3}\psi^3{}_{v_3}(\theta) \tag{11}$$

where $\varepsilon^1{}_{v_1}$, $\varepsilon^2{}_{v_2}$, and $\varepsilon^3{}_{v_3}$ are modal eigenvalues, and v_1, v_2, and v_3 are vibrational quantum numbers associated with coordinates r, R, and θ, respectively. The h_1, h_2, and h_3 are expressed as

$$h_1(r)=-\frac{1}{2\mu_1}\frac{\partial^2}{\partial r^2}+\frac{1}{2\mu_1 r^2}\langle j^2\rangle_\theta+V_1(r)+\langle V_2(r,R,\theta)\rangle_{R,\theta} \tag{12}$$

$$h_2(R) = -\frac{1}{2\mu_2}\frac{\partial^2}{\partial R^2} + \frac{1}{2\mu_2 R^2}\langle l^2\rangle_\theta + \langle V_2(r,R,\theta)\rangle_{r,\theta} \tag{13}$$

$$h_3(\theta) = \langle\frac{1}{2\mu_1 r^2}\rangle_r\, j^2 + \langle\frac{1}{2\mu_2 R^2}\rangle_R\, l^2 + \langle V_2(r,R,\theta)\rangle_{r,R} \tag{14}$$

The subscripts after bracket $\langle\ \rangle$ indicate that the quantity within the bracket is an integral over the modal functions which the subscripts designate. The total SCF energy for the (v_1,v_2,v_3) bound state is

$$E^{\mathrm{SCF}}_{v_1v_2v_3} = \varepsilon^1{}_{v_1} + \varepsilon^2{}_{v_2} + \varepsilon^3{}_{v_3} + E_{\mathrm{cor}} \tag{15}$$

where E_{cor} is

$$E_{\mathrm{cor}} = -\langle\frac{1}{2\mu_1 r^2}\rangle_r\langle j^2\rangle_\theta - \langle\frac{1}{2\mu_2 R^2}\rangle_R\langle l^2\rangle_\theta - 2\langle V_2(r,R,\theta)\rangle_{r,R,\theta} \tag{16}$$

And, of course, the SCF wavefunction is

$$\Psi^{\mathrm{SCF}}_{v_1v_2v_3}(r,R,\theta) = \psi^1{}_{v_1}(r)\psi^2{}_{v_2}(R)\psi^3{}_{v_3}(\theta). \tag{17}$$

We use the numerical grid representations, instead of using the basis function representations, to calculate modal wavefunctions. As we see in Eqs. (12) and (13), the differential equations involving r and R coordinates can be easily integrated. But the coordinate imposes a small problem in numerical representations. To obtain numerical representations for $\psi^3{}_{v_3}(\theta)$, we adopt the discrete variable representation (DVR) proposed by Light and Bacic.[18-20] Light and coworkers have defined a general discrete variable representation for quantum mechanical problems which is a dual space of normal truncated variational basis representations, *i.e.*, it is related by orthogonal (or unitary) transformations. The DVR is established in order to simplify the approximate evaluation and manipulation of the Hamiltonian operator. In particular, the kinetic energy operator, easily evaluated in the variational basis representation, is transformed (exactly) to the DVR, whereas the remaining potential (coordinate) operators, which are difficult to evaluate in the basis representation, are approximated directly (and simply) in the DVR.

In DVR a unitary transformation matrix $\boldsymbol{T}$ is defined as

$$T_{l\chi_\alpha} = \sqrt{(2l+1)/2}\,\omega^{1/2}_{\chi_\alpha}\, P_l(\chi_\alpha) \tag{18}$$

where the square of $\omega^{1/2}_{\chi_\alpha}$ is a numerical weight and $\chi_\alpha(=[\cos\theta]_\alpha)$ is a grid point in angle θ. Then the potential $V(r,R,\theta)$ is approximated to be diagonal(unchanged) in this χ_α basis, but j^2 and l^2 are represented as $\boldsymbol{T}^+\boldsymbol{j}^2\boldsymbol{T}$ and $\boldsymbol{T}^+\boldsymbol{l}^2\boldsymbol{T}$, respectively. The row dimension (l) of $\boldsymbol{T}$ matrix is equal to a number of basis functions when $\psi^3{}_{v_3}(\theta)$ is expanded in terms of Legendre functions, and the column dimension (χ_α) of $\boldsymbol{T}$ is equal to a number of grid points when $\psi^3{}_{v_3}(\theta)$ is expressed in numerical grid representations.

The Eqs. (12), (13), and (14) are all transformed by $\boldsymbol{T}$ matrix to have new equations which are defined numerically. Another words, we calculate a numerical value of $\psi^1{}_{v_1}(r)$, $\psi^2{}_{v_2}(R)$, $\psi^3{}_{v_3}(\theta)$ at each grid point, say, r_α, R_α, and χ_α, respectively. The finite difference method is used to solve the differential equations numerically with the boundary conditions,

$$\lim_{r\to\infty}\psi^1{}_{v_1}(r) = \lim_{r\to 0}\psi^1{}_{v_1}(r) = 0,\quad \lim_{R\to\infty}\psi^2{}_{v_2}(R) = \lim_{R\to 0}\psi^2{}_{v_2}(R) = 0,$$

$$\text{and}\quad \lim_{\theta\to\pi}\psi^3{}_{v_3}(\theta) = \lim_{\theta\to 0}\psi^3{}_{v_3}(\theta) = 0.$$

Each modal function is normalized to unity, *i.e.*,

$$\int_0^\infty \psi^{1*}{}_{v_1}\psi^1{}_{v_1}(r)\,dr = 1,\quad \int_0^\infty \psi^{2*}{}_{v_2}\psi^2{}_{v_2}(R)\,dR = 1,$$

$$\text{and}\quad \int_0^\pi \psi^{3*}{}_{v_3}\psi^3{}_{v_3}(\theta)\sin\theta d\theta = 1 \tag{19}$$

or, numerically,

$$\sum_{r_\alpha=0}^{\infty}[\psi^1{}_{v_1}(r_\alpha)]^2\omega_{r_\alpha} = 1,\quad \sum_{R_\alpha=0}^{\infty}[\psi^2{}_{v_2}(R_\alpha)]^2\omega_{R_\alpha} = 1,$$

$$\text{and}\quad \sum_{\theta_\alpha=-1}^{1}[\psi^3{}_{v_3}(\chi_\alpha)]^2\omega_{\chi_\alpha} = 1 \tag{20}$$

where ω_{r_α}, ω_{R_α}, and ω_{χ_α} are numerical weights for r, R, and θ coordinates, respectively. The SCF equations (9)-(11) are iteratively solved to obtain the converged modal eigenfunctions and eigenenergies for a prechosen reference (v_1,v_2,v_3) bound state.

The vibrational configuration interaction (CI) method is numerically exact. The SCF modal functions form a complete set and therefore the exact wavefunctions for the multimodal system can be expressed in linear combination of products of SCF modal functions (eq. (17)), *i.e.*,

$$\begin{aligned}\Psi^{\mathrm{CI}}_{v_1v_2v_3}(r,R,\theta) &= \sum_{v_1'v_2'v_3'} c^{v_1v_2v_3}_{v_1'v_2'v_3'}\ \Psi^{\mathrm{SCF}}_{v_1'v_2'v_3'} \\ &= \sum c^{v_1v_2v_3}_{v_1'v_2'v_3'}\ \psi^1_{v_1'}(r)\ \psi^2_{v_2'}(R)\ \psi^3_{v_3'}(\theta)\end{aligned} \tag{21}$$

where $c^{v_1v_2v_3}_{v_1'v_2'v_3'}$ is the constant of variational optimization. Such an expansion, by analogy with electronic structure theory, is referred to as a CI wavefunction. The CI method, in principle, produces exact solution of Schrödinger equation (1) and also is independent of the coordinates chosen. In practice the finite number of SCF wavefunctions are used to form CI matrix and the diagonalization of CI matrix generates accurate vibrational energies.

Computational Details

We have used pairwise Morse type potential energy functions. Therefore the whole potential is assumed to be a sum of three pairs of diatomic potentials, *i.e.*, A-B, A-C, and B-C. The relevant Morse parameters, D_e (dissociation energy), β (exponential factor), and r_e (equilibrium distance) are listed in Table 1. The electronic state of both of He-I_2 and He-Cl_2 is the excited B state in which the I_2 or Cl_2 has a symmetry of $^3\Pi_{0^+}$. The atomic masses of He, Cl, and I are 7291, 63746, and 231339 au, respectively.

In numerical integrations of SCF equations, the starting point, the end point, and grid size are repeatedly tested so that optimum number of points are determined. For the bond distance of AB, *i.e.*, r axis, integration is performed from

Table 1. Parameters (au) of Morse type potential energy functions

Pair	D_e	β	r_e
I-I	2.238(−2)[a]	0.9375	5.6995
Cl-Cl	1.433(−2)	1.2450	4.5610
He-I[b]	6.378(−5)	0.6244	7.5590
He-Cl[c]	6.379(−5)	0.8467	6.8030

[a] 2.238(−2)=2.238×10^{-2}. [b] Ref. 24. [c] Ref. 25.

$r=3.0$ (3.0) to $r=15.0$ (20.0) au with a grid of 0.02 (0.05) au for $He\text{-}I_2$ ($He\text{-}Cl_2$). Integration for R axis is from $R=4.0$ (4.0) to $R=25.0$ (30.0) au with a grid of 0.2 (0.2) au for $He\text{-}I_2$ ($He\text{-}Cl_2$). For the two complexes, Legendre functions of $l=0$ to 40 are used for θ axis basis functions. It corresponds to 41 grid points in DVR scheme.

For each vibrational state of (v_1,v_2,v_3) separate SCF calculation is performed. And CI calculation is also repeated for each state. For example, in order to determine the CI vibrational energy of (0,0,0) state, SCF calculation for the (0,0,0) state is performed to generate all necessary modal functions and the CI matrix is constructed with the set of these modals. For another state, *e.g.*, (0,0,1) state, another SCF is performed for the (0,0,1) state and CI calculation is done with the set of modals emanating from the SCF for (0,0,1).

It is important how many SCF configuration (products of modal functions) are included in CI calculations. To perform reliable CI, we have performed "state selection" process. It is composed of many trial calculations in each of which various states are selected. The selection was based on vibrational SCF state energies. The number of selected states is different for each complex and each state. States associated with 25 to 30 v_1 (r) quantum numbers, 2 to 3 v_2 (R) quantum numbers, and 5 to 10 v_3 (θ) quantum numbers are included in CI. It produces CI matrices whose dimension is in the order of 10^3. It may look overly large but it guarantees the convergence of CI calculations. Given the potential energy functions, we believe our CI calculations give almost exact vibrational state energies.

Results and Discussion

Table 2 shows the low lying bound vibrational energy levels of $He\text{-}I_2$ calculated using SCF approximation and CI method. As expected, the stretching mode of I_2 is very strong so that many vibrational states exist. The ground (0,0,0) vibrational state energy turns out to be -4860.84 cm^{-1} from very accurate CI with respect to the complete dissociation limit of three atoms, *i.e.*, He, I, and I. From SCF calculations we obtain the ground state energy of -4860.65 cm^{-1}. The energy gap between the (1,0,0) state and the ground state is calculated to be 125.91 cm^{-1}. Of course this value is slightly smaller than that of diatomic I_2 due to the van der Waals bond formation between I_2 and He. In between (0,0,0) and (1,0,0), several vibrational states are found to exist. Four states with bending modes of He against stiff I_2 are found. Only two of the stretching modes of He against I_2 are found to be bound, *i.e.*, (0,1,0) and (0,2,0). The energy difference between (0,1,0) and (0,0,0) is 8.45 cm^{-1} so that the zero point energy of this stretching mode is about 4.7 cm^{-1}. From the potential we use (see Table 1), the van der Waals interaction energy between He and I_2 is 28 cm^{-1}. Therefore any bound excited stretching mode $(0,v_2,0)$ cannot lie higher by 23 cm^{-1} than the (0,0,0) state. Satisfying this condition, our numerical integration produces only two (0,1,0) and (0,2,0) bound levels. The excitation energy to (0,3,0) from the ground state turns out to be greater than 23 cm^{-1}, which is consistent with the above consideration. So (0,3,0) is not bound. The above analyses are based on very accurate CI results shown in the third column of Table 2. Our CI calculations naturally include all necessary coupling among the three modes.

Table 2. Vibrational energy levels (cm^{-1}) of $He\text{-}I_2$

Vibrational modes	This work			Others	
(v_1,v_2,v_3)	SCF	CI	CI[b]	SCF	CI
(0, 0, 0)	–	–	–	–	–
(0, 0, 1)	5.45	5.27	5.07	7.1	4.9
(0, 0, 2)	8.67	8.36	8.13	9.4	8.7
(0, 0, 3)	9.65	9.52	9.31	not bound	12.4
(0, 0, 4)	11.14	11.04	10.67		
(0, 1, 0)	11.98	8.45	8.25	10.4	12.3
(0, 2, 0)	14.04	11.86	not bound		
(1, 0, 0)	125.91	125.91			

[a] Ref. 26. Exponential-6 potential for He-I with I-I stretching vibration frozen. [b] I-I stretching vibration frozen.

Comparing the SCF (the second column in Table 2) results with the accurate CI ones, one can immediately see that SCF calculations are in reasonably good agreement with CI calculations. For the bending mode of He, the difference between SCF and CI values is less than 1 cm^{-1}. For the I-I stretching mode, SCF and CI values are almost identical. It naturally verifies that strong vibrational motions like I-I stretching mode are hardly affected by mode-mode coupling. In case of the stretching mode of He against I_2 (R-axis, v_2), the difference between SCF and CI is large, *e.g.*, about 3 cm^{-1}. Compared to absolute total vibrational energy, this discrepancy is negligible but, nonetheless, it is important to note that the R-axis stretching mode is very much correlated or coupled with the other I-I stretching and $He\text{-}I_2$ bending modes.

The above calculations are 3-dimensional full calculations. We have also performed 2-dimensional restricted CI calculations in which the stretching vibrational mode of diatomic I_2 is frozen. I_2 is assumed to be at its equilibrium internuclear distance and a rigid rotor. These restricted CI results are listed in the fourth column of Table 2. The (0,0,0) state energy is calculated to be -13.7481 cm^{-1} with respect to the dissociation limit of $He+I_2$. By comparing full 3-dimensional CI with restricted 2-dimensional CI, we note that the vibrational level spacing is almost same in both cases. It gives a piece of important information that the stretching vibrational mode of I-I affects all the ground and excited vibrational motions of He against I_2 by equal amount. Of course, it should be so because the floppy He motion, whatsoever, can not influence much on the stiff I-I motion. According to 3-dimensional CI, the (0,2,0) state is bound but it is not bound in 2-dimensional CI. Even though the coupling between I_2 stretching mode and He motion is small, it can not be simply neglected when the vibrational state lies near dissociation threshold. In vibrational predissociation dynamics study the I_2 stretching motion is often considered to be frozen. But our current study indicates that states near dissociation threshold should be carefully examined when an approximation is imposed.

Horn *et al.* reported SCF and CI calculations for $He\text{-}I_2$

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Hydrogen-Atom and Charge Transfer Reactions within Acetylene/Methanol and Ethylene/Methanol Heteroclusters

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Reactions that proceed within mixed acetylene-methanol and ethylene-methanol cluster ions were studied using an electron-impact time-of-flight mass spectrometer. When acetylene and methanol seeded in helium are expanded and ionized by electron impact, the ion abundance ratio, $[CH_3OH^+]/[CH_2OH^+]$, shows a propensity to increase as the acetylene/methanol mixing ratio increases, indicating that the initially ionized acetylene ion transfers its charge to adjacent methanol molecules within the clusters. Investigations on the relative cluster ion intensity distributions of $[CH_3OH_2^+]/[CH_3OH^+]$ and $[(CH_3OH)_2H^+]/[CH_3OH \cdot CH_2OH^+]$ under various experimental conditions suggest that hydrogen-atom abstraction reaction of acetylene molecule with CH_3OH ion is responsible for the effective formation of CH_2OH ion. In ethylene/methanol clusters, the intensity ratio of $[CH_3OH_2]/[CH_3OH]$ increases linearly as the relative concentration of methanol decreases. The prominent ion intensities of $(CH_3OH)mH$ over $(CH_3OH)_{m-1}CH_2OH$ ions ($m=1$, 2, and 3) at all mixing ratios are also interpreted as a consequence of hydrogen atom transfer reaction between C_2H_4 and CH_3OH to produce the protonated methanol cluster ions.

Introduction

Recent studies on the properties, structures, and reactivities of molecular clusters contribute to an understanding of the chemical dynamics and bonding in systems lying between the gaseous and condensed phases.[1~4] Although the characteristics of the detected ion cluster distribution have often been attributed to the properties and even structural features of the neutral precursors, much less is known about the detailed microscopic processes governed by pairwise molecular interactions and local dynamics.[5,6]

The study of specific chemical reactions within methanol cluster ions has received a great deal of attention since it is possible to observe directly how chemical reactivity changes as a function of stepwise solvation by monitoring the changes in reaction channel versus the cluster size.[7~12] These extensive studies show that the dissociation accompanied by the proton transfer occurring in cluster ions results in efficient production of the protonated ion. Apart from the numerous investigations of the ion-molecule reactions, fragmentations and molecular rearrangements, there are few reported cases of hydrogen transfer mechanisms taking place within the ionized methanol cluster itself.

Our recent investigations of the ion-molecule reactions within methanol containing homo- and heteroclusters[13~15] show that the intracluster proton transfer reactions strongly depend on their relative composition within clusters. In CH_3OH homoclusters, the predominant observation of protonated species, $(CH_3OH)_nH^+$ in the mass spectrum is attributed to the effective formation of ion-neutral complexes, $(CH_3OH)_{n-1}[CH_3OH_2^+ \cdots O(H)CH_2]$ and $(CH_3OH)_{n-1}[CH_3OH_2^+ \cdots OCH_3]$. The formation of protonated species in the mixed ethylene-methanol heterocluster systems, however, is found to be responsible for ethylene molecules within the clusters. In this respect, quantitative investigations on reaction mechanism will be helpful for understanding the proton and hydrogen-atom transfer processes in the gas-phase hydrogen-bonded cluster ions, since no detailed theoretical and experimental studies have been published so far on the mechanisms and energetics of these processes.

In this work, we investigated internal ion-molecule reactions in acetylene-methanol and ethylene-methanol heterocluster systems,[13,14] in which we performed pressure-dependence studies to develop a quantitative interpretation of the reaction mechanisms behind our observations. The observed ion-molecule chemistry of methanol-containing heteroclusters is dramatically affected by the relative concentration of methanol molecules within the clusters. The present results provide further details of intracluster proton and hydrogen-atom transfer reactions, *i.e.*, the roles of ethylene and acety-

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