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A Photoelectron Spectroscopic Estimation of the Concentrations of Simple Hydrogen-bonded Dimers Produced in the Temperature-controlled Supersonic Nozzle Beam

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A photoelectron spectroscopic method is proposed to estimate the ratio of number densities between the monomer and the dimer produced in the supersonic jet. Approximate monomer-dimer ratios have been estimated for water, methanol and formic acid by assuming that the photoionization cross sections of the monomer and dimer are equal to each other. The results show reasonable agreement under similar conditions to those available from mass spectrometric analyses of fragmentation patterns. A simple temperature-controlled supersonic nozzle beam source is described here, which enables us to produce hydrogen-bonded dimers in measurable amounts.

Supersonic nozzle beam technique has recently been drawing a considerable attention not only in the field of molecular beam scattering study but also in various kinds of molecular spectroscopic studies. This seems to be due to the advantageous characters of supersonic nozzle beams which produce molecular clusters (van der Waals molecules, hydrogen-bonded species, *etc.*) with relatively high concentrations and realize low temperature states for internal degrees of molecular freedoms.

Dehmer and Dehmer[1) have first demonstrated the potentiality of this technique in the field of photoelectron spectroscopic studies using inert gas dimers. However, no extensive application of this technique to various chemical species has been published, probably because of the difficulty in controlling the production of their dimers and clusters as well as in analyzing their concentrations quantitatively.

From the chemical points of view, it is important to investigate various kinds of molecular dimers and clusters by photoelectron spectroscopy as well as other molecular spectroscopy. However, in order to apply a supersonic nozzle beam technique to various chemical species which exist in the liquid phase under the normal condition, we have to overcome the following problems. The general criterion to use a supersonic nozzle beam system is to achieve sufficient supersonic expansion under proper stagnation and pumping conditions. For chemical species such as water and many other fundamental chemical compounds, it is essentially important to control the temperature of the whole nozzle beam system both for regulating the vapor pressure stable and for preventing the nozzle from clogging. An electric heating system for the nozzle is not suitable for photoelectron measurements, because of its disturbing electromagnetic field.

In this report we first describe the temperature-controlled supersonic nozzle beam source in detail, which has recently been constructed to measure HeI photoelectron spectra of the water dimer,2) the methanol dimer,3) and the formic acid dimer.4) Secondly, we propose an approximate method to estimate the relative dimer concentration with respect to the monomer concentration from the subtraction procedure between photoelectron spectra of the monomer (reference) and the monomer-dimer mixture. This approach depending on the assumptions is still crude, but it offers a more straightforward interpretation for the dimer concentration than other methods such as mass spectrometry, at least for hydrogen bonded clusters. In the mass analysis of the hydrogen-bonded clusters, it is reported that the fragmentation pattern of these species are rather complicated for the quantitative analysis of neutral concentrations because of a serious protonation in ionization.

Experimental

Design of the temperature-controlled nozzle beam source used in photoelectron measurements is illustrated in Fig. 1. The design and performance of the photoelectron spectrometer combined with this nozzle beam system has been given elsewhere.4) In the measurements discussed in this paper, a disk with a pinhole of 0.1 mm in diameter and 0.5 mm in thickness has been used in the nozzle.

In the present temperature-controlling system, a copper block ($34 \times 34 \times 28$ mm^3) is used as a heat bath for the nozzle, through which a temperature-regulated fluid is circulated. The stainless-steel tubing (8 mm in diameter) is thermally contacted with the heat bath by fastening with screws. The temperature of the top of the nozzle is measured by a copper-constantan thermocouple. A hole of 6 mm in diameter is drilled in the copper block, perpendicular to two parallel holes (6 mm in diameter). The open end of the drilled hole is plugged with a cylindrical block to form a U-shaped tunnel through which the fluid is circulated. The both ends of the U-shaped tunnel are connected with stainless steel bellows (CAJON 1/4″ flexible tubings). The other ends of the bellows are connected to the circulator through the vacuum flange by tubings. All the junctions were carefully brazed to be vacuum tight.

The temperature of the top of the nozzle is controlled by circulating an appropriate fluid from a temperature-regulated bath circulator (NESLAB EX-300). By using water as a circulating fluid, the nozzle temperature is controlled within ±0.3 K between 290 and 370 K. It is possible to raise the nozzle temperature up to about 500 K by using an appropriate circulating fluid and also to lower down to about 250 K by employing a refrigerated circulating bath (NESLAB EN-850). Flowing a cold nitrogen gas, we were able to lower the nozzle temperature down to 175 K in 40 min.

During photoelectron measurements, the vapor pressure of the sample is kept constant by heating a sample container made of stainless steel. Both the container and the pipeline which connects the nozzle to the container can separately be heated by a mantle-shaped heater and a tape heater, respectively. When a 'seeding method' was employed,[4] a carrier gas such as helium or argon was bubbled through a liquid sample in the container. Three pairs of Helmholtz coils are used to compensate the earth's magnetic field, because of the difficulty in covering the ionization and electron energy analyzing regions by μ-metal plates completely.

Results and Discussion

The approximate dimer concentration with respect to the monomer concentration can be estimated from HeI photoelectron spectra by the following way. In the present analysis we consider some two-component (monomer-dimer) systems for which the resulting monomer-dimer ratio seems to be consistent with those of mass spectrometry under similar conditions.[5,6]

The Method of Analysis. Let us consider a series of photoelectron spectra which consist of (a) a normalized spectrum of a monomer-dimer mixture, (b) a normalized spectrum of the pure monomer (reference), and (c) the stripped spectrum, as illustrated schematically in Fig. 2. The first two spectra (a) and (b) in Fig. 2 are obtained directly from the photoelectron measurements followed by intensity normalization at the maxima. In the mixture spectrum (a), the ratio of the band area (S_d/S_m) between the first bands of the dimer and the monomer, for instance, should reflect the ratio of the concentrations between the dimer and the monomer in the supersonic jet. The stripped spectrum (c) is obtained in such a way that the intense monomer band in the mixture spectrum (a) should be reasonably cancelled by subtraction of the reference spectrum (b) with a proper factor α. In other words, the following relationship holds for the photoelectron intensity curves which are given as a function of the photoelectron kinetic energy (E).

$$I_s(E) = I_m(E) - \alpha I_r(E), \tag{1}$$

where $I_m(E)$, $I_r(E)$, and $I_s(E)$ are the photoelectron intensities of the mixture spectrum, the reference spectrum and the stripped spectrum, respectively.

The number densities of the monomer (N_m) and the dimer (N_d) in the beam should be proportional to the band areas S_m and S_d, respectively, as can be expressed by the following equations.

$$S_m = \alpha \int_{\text{band}} I_r(E)\mathrm{d}E = \alpha k_m \sigma_m N_m, \tag{2a}$$

and

$$S_d = \int_{\text{band}} I_s(E)\mathrm{d}E = k_d \sigma_d N_d, \tag{2b}$$

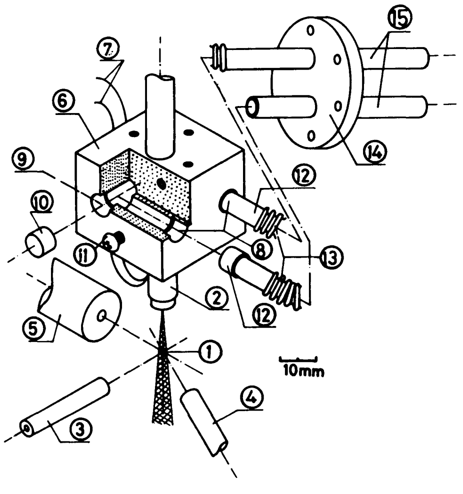

Fig. 1. A schematic drawing of the construction of the temperature-controlled supersonic nozzle beam source: (1) ionization region, (2) nozzle pipe, (3) glass capillary for the light beam, (4) copper tubing for the effusive source, (5) the first piece of an electrostatic lens system, (6) copper block heat bath, (7) copper-constantan thermocouple, (8) two parallel holes, (9) hole connecting the two parallel holes, (10) plug, (11) screw to fasten the nozzle pipe with the heat bath, (12) braze adopters, (13) bellows, (14) vacuum flange, and (15) tubings connected with the fluid circulator.

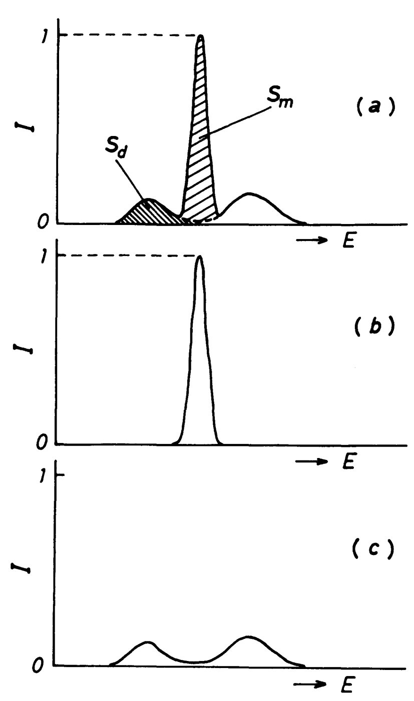

Fig. 2. An illustrative representation of the relation among (a) a normalized photoelectron spectrum of the monomer-dimer mixture ($I_m(E)$), (b) a normalized reference (monomer) spectrum ($I_r(E)$), and (c) the stripped spectrum: $I_s(E)=I_m(E)-\alpha I_r(E)$. Photoelectron intensity in each spectrum is a function of the kinetic energy (E). The monomer and dimer contributions (the shaded areas in spectrum (a)) are indicated by S_m and S_d, respectively.

TABLE 1. APPROXIMATE DIMER CONCENTRATIONS ESTIMATED FROM THE PHOTOELECTRON MEASUREMENTS

	Estimated dimer/monomer ratio[a]	Stagnation condition[b] T/K	Stagnation condition[b] P/Torr	Ref.
Water	0.06	335	390	2
Methanol	0.2	295—320	100—260	3
Formic acid	3	298	20+130(He)	4

a) Probable errors depend on the validity of the assumptions (see text). b) An aperture of 0.1 mm in diameter is used for the nozzle.

where σ_m and σ_d are the total photoionization cross sections of the monomer and the dimer, respectively. The constants k_m and k_d represent the difference in the angular distribution of photoelectrons, since the photoelectron transmission efficiencies at the same kinetic energy for the monomer and the dimer are equal to each other. It is easily noted from consideration of the differential photoionization cross section⁷⁾ that the ratio k_d/k_m would never exceed a factor of two even in the extreme case, when photoelectrons are measured at 90° with respect to the photon beam as in the present case.** Provided that the difference in the angular distribution is negligibly small, the monomer-dimer number density ratio is simply given by

$$N_d/N_m = \alpha(S_d\sigma_m/\sigma_d S_m). \quad (3)$$

Since we have no established knowledge on the ratio of σ_m and σ_d, let us assume $\sigma_d = \sigma_m$ to the crudest approximation. The resulting equation can give the order of the magnitude of the monomer-dimer number density ratio in the sample jet,

$$N_d/N_m \approx \alpha(S_d/S_m). \quad (4)$$

Results of Estimation. The relative dimer concentrations for water, methanol, and formic acid estimated from the previous measurements with a nozzle pinhole of 0.1 mm in diameter are summarized in Table 1, along with the stagnation conditions.

Before making a quantitative comparison between our photoelectron spectroscopic estimation and the available mass spectrometric analysis, we should note the following points.

(1) Production of the dimeric and polymeric species depends on the stagnation conditions and the nozzle characteristics (the shape and the size of the aperture and the depth of the throat), which are different in various studies. Therefore, in order to make proper comparisons of the results, the following experimental conditions should be specified: (a) the diameter and the depth of the aperture of the nozzle (the latter is sometimes not indicated in literatures) and (b) the stagnation pressure and temperature and also the composition of gases if the seeding method is applied.

(2) Fragmentation patterns of the hydrogen-bonded clusters in mass spectrometry seem to be rather complicated, depending on the ionizing projectile (electrons or photons) and its impact energy. No quantitative method to identify the original components from the relative abundance of the ions has been established yet. Under the condition where concentrations of higher polymers are negligible, however, the intensity ratio of the protonated ions (MH^+) or the sum of the protonated ion (MH^+) and the parent ion (M_2^+) with respect to the parent monomer ion (M^+) can be regarded as reflecting the neutral monomer-dimer ratio as a crudest approximation, since hydrogen-bonded dimers yield protonated monomer ions (MH^+) predominantly.⁵⁾,⁶⁾,⁸⁻¹¹⁾

Our monomer-dimer ratio for the water (6%) is in good agreement with the result of the ion intensity ratio ($H_3O^+/H_2O^+ \approx 10\%$) reported by Dyke *et al.*⁵⁾ under the similar condition. For the methanol dimer, Odutola *et al.*⁶⁾ obtained a value of 8% for $(CH_3OH)H^+$ and 4% for $(CH_3OH)_2^+$ with respect to $(CH_3OH)^+$ under the stagnation condition of 317 K and 100 Torr (1 Torr=133.322 Pa). This result also shows a reasonable agreement with our present estimation. Cook *et al.*⁸⁾ have recently suggested larger relative concentrations of the dimer to higher polymers for methanol. However, their results cannot be compared directly with our present estimation, because their nozzle (conical, 0.33 mm in diameter) quite differs from ours both in the shape and size of the aperture.⁹⁾

Our estimation of the dimer concentration for the formic acid gives a quite large value which means about three times more dimers than the monomer in the supersonic jet. There seems no available data on the mass analysis of the formic acid dimer for direct comparison. Recently, the temperature dependence of cluster formation for some carboxylic acids in the supersonic jet has been studied by Cook *et al.*¹⁰⁾ and by Mori *et al.*¹¹⁾ by means of mass spectrometry. These studies have indicated that the dimer formation is extremely dominant for these cyclic dimers and it behaves as a monomer-dimer equilibrium mixture even in the supersonic jet. Therefore, it may be reasonable to understand the high dimer concentration of the present estimation for the formic acid as a "quasi-equilibrium" at a reduced pressure,⁴⁾ since about ten times higher dimer concentration (monomer : dimer =10% : 90%) is expected for the saturated formic acid vapor (about 40 Torr at 298 K) from the equilibrium constant by Coolidge.¹³⁾

Conclusion

(1) By using the approximate method described above, the monomer-dimer number density ratio in the supersonic jet has been deduced from careful examinations of the stripping procedure involved in the photoelectron data analysis. The estimated values show reasonable agreements with the available results of mass spectrometric analysis.

(2) The deduction of HeI photoelectron spectra for some hydrogen-bonded dimers has clearly demonstrated the importance and the potentiality of the temperature-controlled nozzle beam source. The present nozzle system is especially suitable for electron spectroscopic measurements, because it is free from electromagnetic fields around the ionization region.

(3) A variety of its applications to molecular beam experiments may be expected not only for electron spectroscopic studies but also for other spectroscopic studies, especially because of its simple structure.

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** The angular distribution of photoelectrons is given by the following equation,

$$d\sigma(\theta)/d\Omega = (\sigma_{tot}/4)[1-(\beta/4)(3\cos^2\theta-1)],$$

where σ_{tot} is the total photoionization cross section and β is the asymmetry parameter which ranges from −1 to 2.

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