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Vacuum UV Photoelectron Intensity of Gaseous Compounds. II. Experimental Processes of Determination of Differential and Partial Photoionization Cross Sections

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Experimental processes recently developed to determine differential and partial photoionization cross sections of molecules are described in detail, based on photoelectron intensity measurements using a gaseous binary mixture of a sample with a standard gas. The quantities obtained here in these processes are 1) relative photoelectron peak heights, 2) normalized photoelectron spectra, 3) relative photoelectron band areas, and 4) differential and partial photoionization cross sections. Corrections are made for electron collecting efficiency. In connection with the photoelectron intensity determination, we propose here a method of obtaining the mole ratio of the components of a binary mixture entered into the ionization chamber of a photoelectron spectrometer. Satisfactory results on partial photoionization cross sections have been obtained for several testing samples.

In molecular photoelectron spectroscopy, much attention has been devoted to studies of ionization energies rather than photoelectron intensities, so that its quantitative character is still very poor. It seems quite important to study relative photoelectron intensities from molecule to molecule not only analytical points of view but also theoretical points of view. If intensity-normalized spectra for a number of molecules are obtained with respect to a certain peak of a standard molecule, photoelectron spectroscopy will strengthen its ability as an analytical tool. On the other hand, the band intensity for each photoelectron band is closely associated with the partial photoionization cross section or the branching ratio which is the probability of producing a specific ionic state, so that experimental intensity data are important for testing theoretical models of photoionization processes.

Previously we have reported an essence of our photoelectron intensity determination, together with some preliminary results of its application to simple molecules.[1] Since then we have been developing the system using a mini-computer based data-processing system.

The purpose of the present paper is to describe our detailed processes of intensity determination which were not reported in our previous paper.

Most of photoelectron intensity works published so far have been limited to relative band intensities within molecule for various molecules.[2–4] Concerning relative band intensities among different compounds, only several works have been published in which rare gas atoms and several simple molecules are treated.[5–9]

This may be partly due to serious requirement for the knowledge of various instrumental parameters in comparing photoelectron intensities among different molecules.

Partial photoionization cross section of a molecule can be determined by combining the total photoionization cross section and branching ratios. The total photoionization cross section has traditionally been obtained from optical absorption measurements,[10,11] while the branching ratio can be obtained from photoelectron intensity measurements. Combining optical absorption data with photoelectron intensity data, Blake and Carver[12,13] earlier obtained partial photoionization cross sections (as a function of the incident photon energy) for several simple compounds. Samson[10] has proposed a method of using a double ionization chamber to obtain total photoionization cross sections, and they have determined partial photoionization cross sections for several simple molecules at various photon energies. This is probably the most orthodox method of determining the partial photoionization cross section.

Kemeny *et al.*[8,9] have first shown the use of photoelectron intensities of binary mixtures to determine partial photoionization cross sections of the rare gas atoms (Ar, Kr, and Xe), using a relation of the inverse square root of mass to determine mole fractions of the binary mixture. However, such correction may not be always valid for molecules, especially for large molecules. It seems to be important to determine experimentally the real mole fractions of each binary mixture entered into the ionization chamber of a spectrometer.

In order to obtain partial photoionization cross sections for various molecules, we have recently developed our own experimental system applicable to a wide range of molecules, which is somewhat similar to that of Kemeny.[8,9] In the present work we have established an experimental procedure of determining mole fractions of a binary mixture entered into the ionization chamber.

Principle of the Method

The differential photoionization cross section $I_j(\theta) = d\sigma_j/d\Omega$ for producing the jth ionic state in the solid angle $d\Omega$ at the angle θ for unpolarized light is related to the corresponding partial photoionization cross section σ_j by[10]

$$I_j(\theta) = (\sigma_j/4\pi)\{1-(\beta_j/4)(3\cos^2\theta-1)\}, \quad (1)$$

where θ is the angle between the incident photon, beam and the direction of photoelectron detection and β_j is the asymmetry parameter.

When photoelectron measurements are carried out with a pulse counting technique under conditions that the gas pressure is kept constant in the ionization chamber and electron scattering by the gas is not significant, the number of counts per unit time at the jth photoelectron band may be expressed by

$$N_j \propto I_0 n S I_j(\theta) C(E_j), \qquad (2)$$

where I_0 is the incident photon flux, n is the density of molecules in the effective ionization volume, S is the sample factor, and $C(E_j)$ is the spectrometer collecting efficiency for electrons with kinetic energy E. The relation (2) is the same as represented by Gardner and Samson[14] except for S which should be taken into account since sensitivity of a channeltron depends more or less on gaseous samples.

For a binary mixture of A (standard) and B (sample), the following formula can be obtained from the relation

$$\frac{N_j^B}{N_1^A} = \frac{n^B I_j(\theta)^B C(E_j)^B}{n^A I_1(\theta)^A C(E_1)^A} \qquad (3)$$

(2) under the same apparatus conditions. Using this relationship we can obtain the relative intensity of the jth band of B with respect to the first band of A. The advantage of this method is that the both instrumental factors I_0 and S are excluded in Eq. 3. If the mole fraction of the binary mixture and the electron collecting efficiencies are known, then differential photoionization cross sections I_j^B can be obtained relatively with respect to I_1^A. Furthermore, partial photoionization cross sections may also be evaluated relatively with respect to σ_1^A, if assymmetry parameter β_j^B are known. Therefore, differential and partial photoionization cross sections of molecules may be determined in absolute values on the basis of those of the standard molecule.

Experimental

Apparatus. A block diagram of the whole experimental apparatus is shown in Fig. 1. All of the gas inlet system, the data-processing system, and data-recording system have been constructed for the present purposes. A HeI photoelectron spectrometer with a hemispherical electrostatic analyzer is essentially the same as used previously.[15]

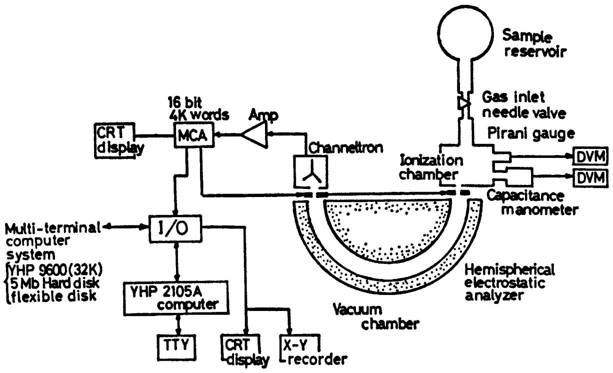

Fig. 1. A block diagram of the photoelectron spectrometer and the data-processing system.

The sample reservoir system is attached to the ionization chamber across a variable leak valve, consisting of three 2-*l* glass bulbs in which binary gaseous mixtures of the sample and the standard (mainly, N_2) were filled with different mole ratios at total pressures of about 50 Torr. The ionization chamber (20×20×30 mm) has a rectangular slit (0.4 mm × 10 mm) through which photoelectrons are emitted. The sample gas introduced into the ionization chamber is evacuated also through this slit. The sample pressure in the ionization chamber was monitored with two kinds of different pressure gauges, one of which is an MKS Baratron pressure gauge (Model 220) and the other is an Edwards Pirani gauge (Model 11). Outputs of the two pressure gauges were fed into the data processing system.

Photoelectron measurements were carried out by varying accelerating/retarding voltages on the analyzer entrance slit in synchronization with the channel-advance clock of the multichannel analyzer. Pulse signals detected by a channeltron electron multiplier were preamplified and shaped, and then counted by a multichannel analyzer with 16 bit-4K words. Intensity data stored in the multichannel analyzer were then transferred to a minicomputer (Model YHP 2105A) through input-output interfaces (I/O) for further data processing. Numerical data of normalized photoelectron spectra were stored in a floppy disk through an online-multiterminal computer system (Model YHP 9600) of the Institute of Applied Electricity, Hokkaido University.[16] In this computer system, the programming is allowed in only FORTRAN language by using some PROMs for code conversions.

Determination of Mole Fraction. In the present gas inlet and outlet systems, it is considered that the mole fraction of the binary mixture in the ionization area differs from that in the gas reservoir. This is probably true for commonly used photoelectron spectrometers. (In such a gas flowing system there may be some deviation in the mole fraction from the law of the inverse square root of the mass.)

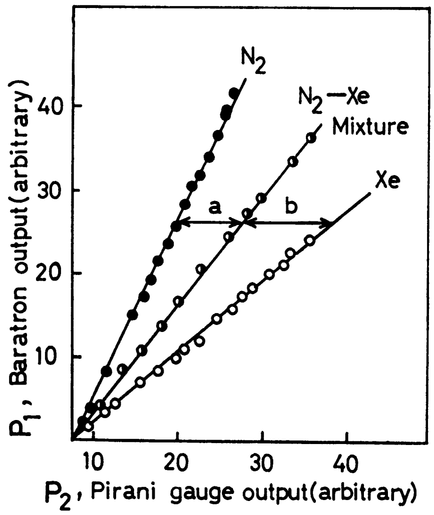

Fig. 2. Plots of the Baratron and Pirani outputs measured for Xe, N_2, and Xe–N_2 mixture, indicating that the mole ratio in the ionization chamber is given by a:b. (The initial mole ratio of Xe to N_2 in the mixture in the gas reservoir was 1 : 3 in the present case.)

An example of the mole fraction determination is illustrated in Fig. 2, in which various output data of the Baratron gauge are plotted against those of the Pirani gauge in the case of a binary mixture of N_2 and Xe. The three kinds of plots in Fig. 2 show approximately linear lines with different slopes in the pressure range studied. The partial prassures of Xe and N_2 should be proportional to a and b in Fig. 2, respectively.

Electron Collecting Efficiency Curve. Since the electron collecting efficiency $C(E)$ depends on the photoelectron energy, it is necessary to construct a curve of $C(E)$ as a function of E

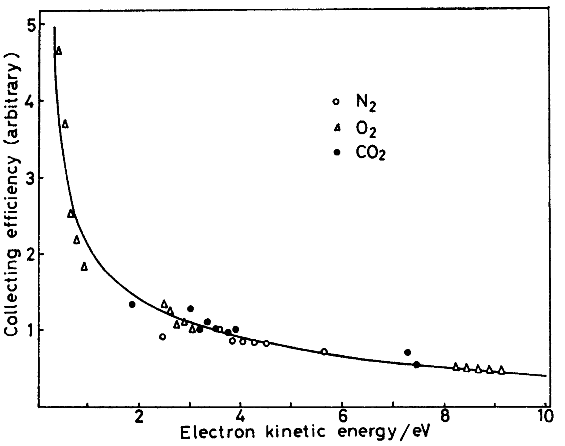

Fig. 3. The electron collecting efficiency curve of the photoelectron spectrometer used here. The solid curve was obtained by a least squares fitting.

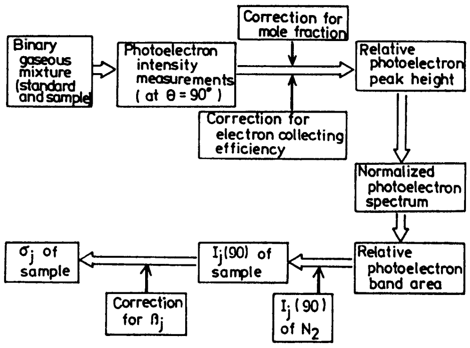

Fig. 4. A flowchart for the determination of differential and partial photoionization cross sections.

in order to obtain real photoelectron intensities. In the present work a curve of $C(E)$ was constructed by correlating our photoelectron peak intensities of N_2, O_2, and CO_2 with the corresponding data of Gardner and Samson.[17] Many typical data thus obtained for electron collecting efficiency are plotted in Fig. 3, the solid curve being obtained by a least-squares fitting with a fifth-order polynominal. The standard error involved is about 4% below 19 eV, while it is 15% above 19 eV.

Data Processing. All the processes included in the determination of differential and partial photoionization cross sections are shown by a flowchart in Fig. 4. Experimental data obtained from HeI spectrum in this scheme are : 1) relative peak heights with respect to the nitrogen first peak, 2) normalized spectra, 3) relative band areas with respect to the nitrogen first band, 4) differential photoionization cross sections, and 5) partial photoionization cross sections. During these processes, corrections are made for 1) the mole fraction of the binary mixture in the ionization area, 2) the electron collecting efficiency of the spectrometer, and 3) the photoelectron angular distribution. In the evaluation of differential and partial photoionization cross sections of molecules, a value of $I_1(90)=0.78\pm0.05$ Mb of the nitrogen first band was used as a reference, that is derived from Eq. 1 with $\sigma_1=8.4\pm0.3$ Mb and $\beta_1=0.68\pm0.05$ reported by Samson *et al.*[18]

Normalized Photoelectron Spectra. HeI 'normalized' photoelectron spectra were obtained with respect to the first photoelectron peak of N_2. Some examples of the normalized spectra are shown in Fig. 5. Photoelectron intensity measurements were carried out several times repeatedly for each photoelectron band with a reproducibility within 3%. Background

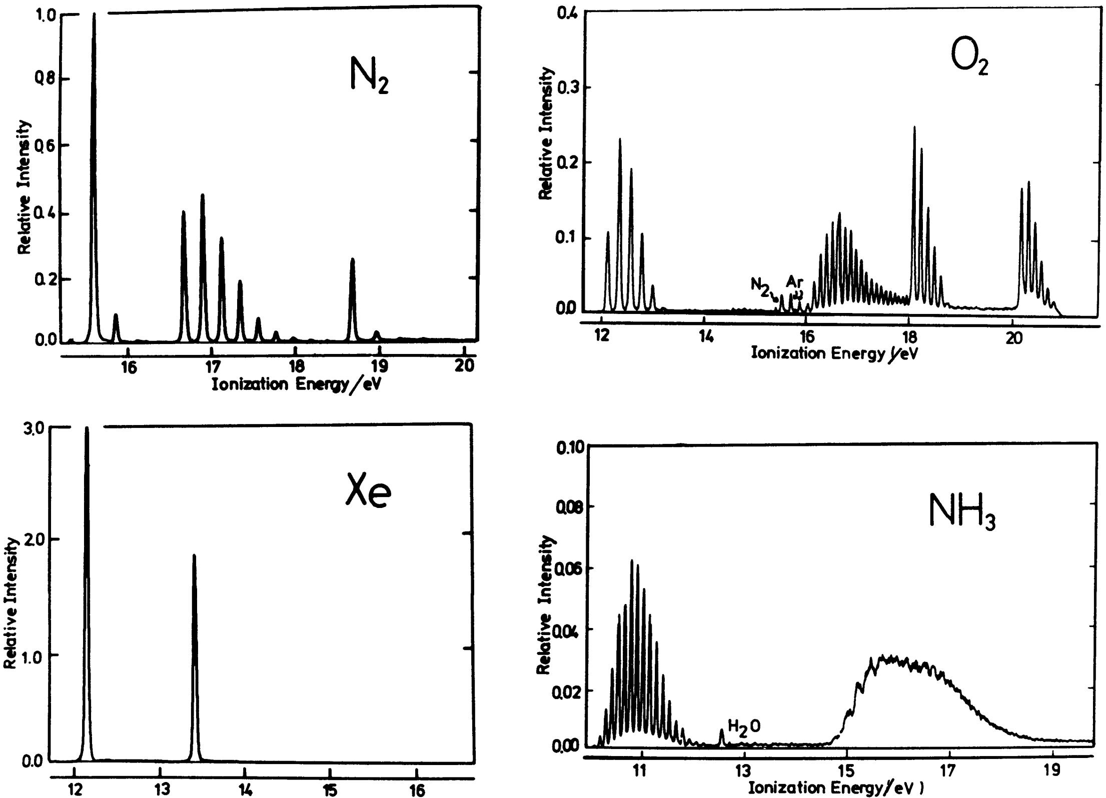

Fig. 5. HeI normalized photoelectron spectra obtained here for N_2, Xe, O_2, and NH_3. The first peak of N_2 is taken as unity. (The spectra were obtained at 90° with respect to the unpolarized light.)

signals were subtracted prior to the normalization process of HeI spectra.

Results and Discussion

Separation factors obtained here for several binary mixtures with an original mole ratio of 1 : 1 are summarized in Table 1, compared with those estimated from the law of the inverse square root of the mass. It is seen from Table 1 that there is a large discrepancy only in the case of benzene, while good agreements are obtained in the other cases, even in rather extreme cases of H_2 and Xe which largely differ from N_2 in the masses. For large molecules such as benzene, such mole fraction determinations are especially important. Probably a more or less similar situation occurs for other conventional spectrometers. It is desirable to construct a new apparatus with a molecular-beam gas inlet system for photoelectron intensity measurements, since the mole fraction separation of binary mixture completely obeys the law of the inverse square root of the mass of its component.

TABLE 1. RATIOS OF PARTIAL PRESSURES OF BINARY MIXTURES IN THE IONIZATION CHAMBER (THE INITIAL MOLE RATIO IN THE GAS RESERVOIR IS 1 : 1)

Mixture (A+B)	$(p_B/p_A)^{a)}$	$(\sqrt{m_B/m_A})^{b)}$
N_2+Ar	1.2	1.2
N_2+Kr	1.6	1.7
N_2+Xe	2.1	2.2
N_2+H_2	0.27	0.27
N_2+CH_4	0.81	0.76
N_2+NH_3	0.78	0.78
N_2+benzene	1.0	1.6

a) p_A and p_B are the partial pressures of A (N_2) and B (sample), respectively, in the ionization chamber.
b) m_A and m_B are the masses of A (N_2) and B (sample), respectively.

TABLE 2. PARTIAL PHOTOIONIZATION CROSS SECTIONS (σ_j/Mb) OF THE RARE GAS ATOMS (Ar, Kr, AND Xe) AT 58.4 nm

Atom	This work	Samson and Cairns[19]	West and Marr[20]	Kemeny *et al.*[8,9]
Ar	37.1	36.4	36.5	36.4
Kr	39.2	36.5	35.7	42.6
Xe	32.0	29.5		33.3

It should be mentioned that there are some gases such as CO which is very similar in the Baratron-Pirani curve to N_2. In such cases another gas instead of N_2 should be selected as a standard.

Partial photoionization cross sections obtained here at 58.4 nm are summarized in Table 2, together with available data.[8,19,20] The purpose of studying the rare gas atoms in the present work is only to test the validity of the whole procedure proposed here. As can be seen from Table 2, satisfactory results have been obtained.

Only the HeI resonance line has been used in the present work. The purpose of this was to establish the whole system at first. Samson *et al.*[18] have recently studied energy dependence of partial photoionization cross sections for several simple compounds by a combination of photoelectron spectroscopy and ion current measurements, using a variety of resonance lines through a monochromator. Brion *et al.*[21] have also studied the energy dependence for several simple molecules, using an electron impact ionization technique. Synchrotron radiation is of course a very useful source to carry out such studies in wide energy range. The present method proposed here may be applicable to any light sources, and its future application to various molecules with synchrotron radiation seems to be very interesting.

The advantage of the present method is that the partial photoionization cross sections of molecules can be obtained from only photoelectron intensity measurements with a conventional photoelectron spectrometer. It is also desirable to carry out photoelectron measurements at the magic angle rather than at right angle as already pointed out by Samson.[10]

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