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Photoemission of Ion Radical Salts. Benzonitrile- and Triphenylene-Alkali Metal Complexes

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The photoelectric emission of the benzonitrile-alkali metal salts were measured and compared with those of the hydrogen-chemisorbed samples. The adsorption of hydrogen onto the salt caused a decrease in the quantum yield of the photoemission at a higher energy region and also a decrease in the threshold energy. The threshold energies were 5.05±0.02 eV for the benzonitrile-rubidium ion radical salt and 4.95±0.02 eV for its hydrogen-chemisorbed sample. Further, the spectral response of the quantum yield of the photoemission for the triphenylene-cesium complex was measured. The threshold energies of the mono- and dinegative ions were 2.40 eV and 2.43 eV respectively, and the quantum yield of the mononegative salt was ten times than that of the dinegative one.

The photoemission from inorganic solids—metals and semiconductors —— has been studied by many workers. However, few studies have been reported on the photoemission from organic materials, especially for organic complexes. Suhrmann first showed that the efficiency of the photoelectric emission of alkali metals is enhanced by the evaporation of hydrocarbon, naphthalene, or anthracene onto sodium (or potassium) metal film;[1] this enhancement may arise from the formation of a complex between alkali metal and aromatic hydrocarbon.

Since this pioneer work, several studies of the photoemission from the aromatic-alkali metal salts have been made in order to clarify the mechanism of the charge-transfer process of the complexes.[2,3]

In this paper, we will present out results on the photoemission from the ion radical salts, benzonitrile-alkali metals and triphenylene-alkali metal. The effect of hydrogen adsorption onto the surface of the benzonitrile-alkali metal complex on the photoemission will be discussed. Further, the change in the photoemission efficiency from the triphenylene-alkali metal salt as a function of the valencies of the aromatic anion is reporsed.

Experimental

Preparation of the Thin Film of the Ion-radical Salt. *Benzonitrile-alkali metal salts*[4]: Commercial benzonitrile was refluxed with diphosphorous pentoxide in a sealed glass vessel to eliminate all traces of water, subsequently degassed by alternate boiling under a vacuum, and distilled repeatedly. Cesium and rubidium metals, the electron donors, were prepared from their chlorides by reduction with calcium metal in an evacuated glass vessel.[5] The sodium metal was purified by distillation *in vacuo*.

Both the preparation of the ion-radical salt and the measurement of the photoemission from the salt were carried out *in vacuo* ($10^{-5}-10^{-6}$ Torr) because of the instability of the ion-radical salt in air; the purified alkali metal was first evaporated on the surface of a glass vessel, and then purified benzonitrile liquid was introduced into the vessel. By these operations, a dark red solution (excess benzonitrile acts as a solvent) was made. The coloured solution was then dropped onto a copper-disc cathode (emitter) 10 mm in diameter, and the excess benzonitrile was evaporated completely for about 20 hr to make the radical-salt thin film. Then, the copper disc with the deposited salt film was moved towards the centre of the glass photocell, the inside of which had been coated with evaporated gold thin film and which was used as collector. Figure 1 shows the delicate glass photocell.

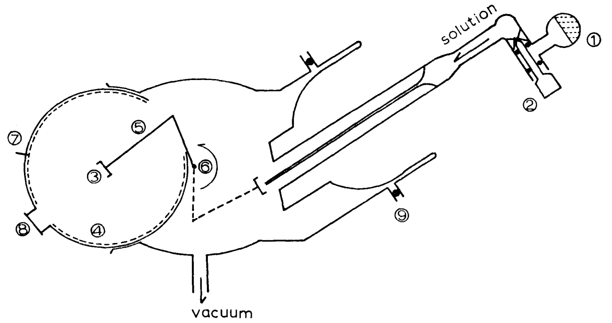

Fig. 1. The schematic diagram of the apparatus for photoemission measurement *in vacuo*. (1); The ion salt solution, (2); greaseless tap, (3); copper disc with the film, (4); Au evaporated film, (5); copper rod, (6); tungsten rod and moving apparatus, (7); collector lead (tungsten rod), (8); quartz window, (9); O-ring.

Triphenylene-cesium ion-radical salt: Commercial triphenylene was recrystallized several times from its alcohol solution and then sublimed in a vacuum. The triphenylene-cesium complexes, both mono- and dinegative ion salts, were prepared as precipitates from their tetrahydrofuran (THF) solution when the triphenylene in THF was brought in contact with Cs metal.[6] The THF solution, in which the radical salt had been suspended, was dropped onto the copper disc through a glass capillary, and then the THF was completely evaporated from the solution, during about a 4 hr period, to make a thin film.

Measurement of the Photoemission. An incident light from a hydrogen-discharge lamp was monochromatized with a Hilger-type monochromator with a quartz prism (for the benzonitrile salt) and also with a Shimadzu Baush-Lomb monochromator (for the triphenylene salt). The absolute measurement of the light intensity was made by means of an

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[1] R. Suhrmann, *Z. Phys.*, **94**, 742 (1935), **111**, 18 (1937).

[2] H. Inokuchi and Y. Harada, *Nature*, **198**, 477 (1963); T. Hirooka, M. Kochi, J. Aihara, H. Inokuchi, and Y. Harada, This Bulletin, **42**, 1481 (1969).

[3] M. Batley and L. E. Lyons, *Mol. Cryst.*, **3**, 357 (1968).

[4] M. Tsuda and H. Inokuchi, This Bulletin, **43**, 3410 (1970).

[5] $2MCl+Ca=2M+CaCl_2$ (M=Cs and Rb).

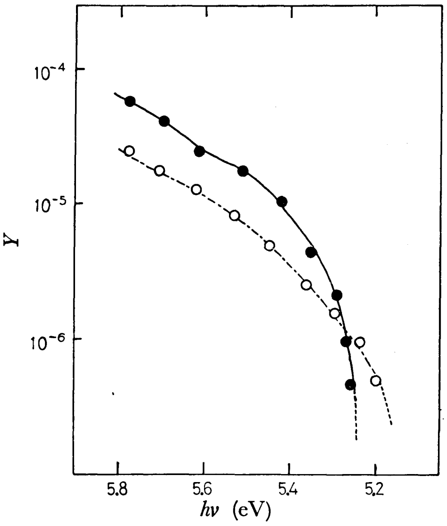
[6] The triphenylene-Cs ion radical salt was precipitated as deep-coloured crystallites; in the salt, triphenylene forms mono- and dinegative ions, depending on the amount of alkali metal. The details will be reported elsewhere.[7]

[7] K. Kimura and H. Inokuchi, to be published.

Epply circular thermopile, the sensitivity of which was 0.3 μV/μW *in vacuo*. The output potential was applied from a Keithley 241 voltage supply; 10 V for the benzonitrile salt[8] and 50 V for the triphenylene salt. The photoemissive current was amplified and measured by means of a Cary 32 vibrating-reed electrometer, as a function of the wavelength of the incident light.

Results and Discussion

Benzonitrile-Alkali Metal Salts. The photoemissions from the benzonitrile-sodium, rubidium, and cesium ion-radical salts were measured as functions of the wavelength of the incident light; at first, the measurement of the photocurrent of the freshly prepared film was carried out, and then the salt film was placed in contact with purified hydrogen gas of 10 Torr for 100 min and then pumped up to 10^{-5} Torr. The photocurrent from the hydrogen-exposed film was measured and compared with that of the fresh one.[9] Figures 2, 3, and 4 show the photoelectric yield curves as functions of the photon energy.



Fif. 2. The spectral distribution of the quantum yield for the Na-Benzonitrile film -●- and for its hydrogen-exposed film -○--.

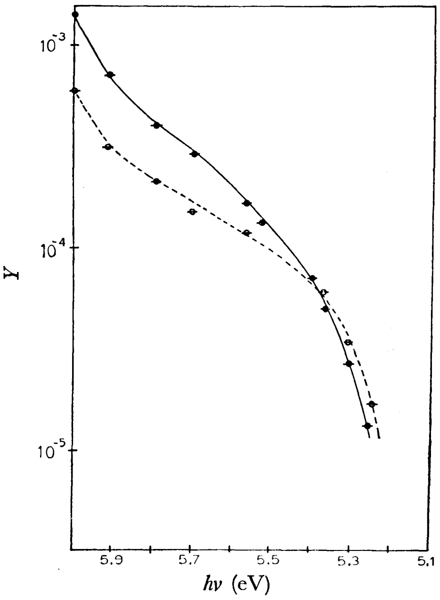


Fig. 3. The spectral distribution of the quantum yield for the Rb-Benzonitrile film -●- and for its hydrogen-exposed film -○--.

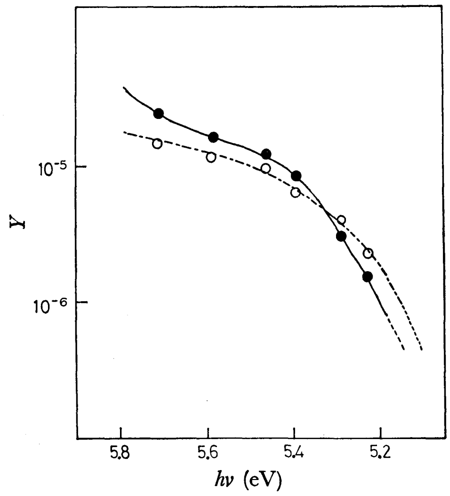


Fig. 4. The spectral distribution of the quantum yield for the Cs-Benzonitrile film -●- and for its hydrogen-exposed film -○--.

In the present work, the quantum yield (in electrons/quantum unit) was measured only down to 10^{-6}; thereafter, the threshold energy, E_{th}, could not be determined by an extrapolation method.[10] Therefore, the value of the threshold energy had to be obtained another method. By analogy with the Fowler plots for the photoemission of metals, the quantum yield of the ion radical salts near the threshold energy may be subjected to the conventional power law:

$$Y \propto (E-E_{\text{th}})^n \qquad (1)$$

where Y is the quantum yield and E is the incident

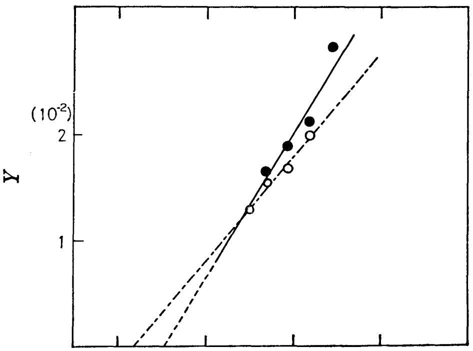


Fig. 5. The power-law fit for the photoelectric quantum yield near the threshold region (Cs-benzonitrile salt).
for the fresh film -●- and
for the hydrogen-exposed film -○--.

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[8] The applied voltage was enough for a saturated photoemissive current to be found.

[9] H. Kawamura, M. Tsuda, and H. Inokuchi, *Chem. Phys. Lett.*, **5**, 80 (1970).

[10] The values of E_{th} are determined by extrapolation from a quantum yield of 10^{-7}—10^{-9} electrons per incident quantum.

photon energy. For the organic complexes, it has been shown empirically that a cube-root plot of the quantum yield ($n=3$) becomes almost linear as a funciton of the incident photon energy, as is illustrated in Fig. 5.[2,11] Table 1 summarizes the values of E_{th}. In Table 1, the accuracy of the work function of the salts is kept within the range of the resolving power of the monochromator for an incident light; the resolving power is 0.02 eV. The values of E_{th} thus obtained are, for example, 5.05 ± 0.02 eV for the benzonitrile-Rb ion radical salt and 4.95 ± 0.02 eV for the H_2-exposed sample. The energy differences, ΔE, between the fresh sample and the H_2-exposed one are 0.07—0.1 eV.

TABLE 1. THE THRESHOLD ENERGY in eV OF PHOTOEMISSION OF BENZONITRILE-ALKALI METAL ION RADICAL SALTS

Donor	Fresh	H_2-exposed	ΔE
Na	5.01	4.92	0.09
Rb	5.05	4.95	0.10
Cs	5.11	5.04	0.07

Generally, in the formation of the salt there is a sharp increase in the electronic conductivity and in the quantum yield photoemission in comparison with its components. The mobile electrons in the salt may originate from the excess charge which transfers from the donor, the alkali metal, to the acceptor, aromatics. The adsorption of hydrogen causes a decrease in the quantum yield in the higher energy region and also a decrease in the threshold energy, as is illustrated in Figs. 2—4. A similar phenomenon appeared in the behavior of the electronic conductivity; that is, there was a marked decrease in the conductivity with the chemisorpition of hydrogen onto the ion-radical salt.[12] The above findings suggest that the excess charge of the radical salt participates in forming a chemisorption-bond with hydrogen.

The quantum yield near the threshold energy of the H_2-exposed sample was larger than that of the fresh one, and the work function of the salt was decreased by the adsorption of hydrogen gas. It seems that the dcrease in the work function derives from the appearance of the surface state, located 0.07—0.1 eV[13] above the highest occupied level of the salt. When the hydrogen-exposed sample was pumped out for a week, the value of the quantum yield of the H_2-exposed sample recovered the value of the fresh sample. Figure 6 shows the time dependence of the photoemission for the benzonitrile-cesium complex under pumping.[14] This result shows that the hydrogen is chemisorbed onto the salt, but does not react.

Triphenylene-Cesium Complex. Figure 7 shows the quantum yield curve of photoemission for the triphenylene-cesium complex. The threshold energies of the mono- and dinegative ion salts are 2.40 and 2.43 eV respectively. The quantum yield of the mononegative salt is ten times that of the dinegative one. In the case of the dinegative solid, there are many cesium ions surrounding the aromatic anion; therefore, it is more difficult for the electrons to jump out than in the case of the mononegative sample.

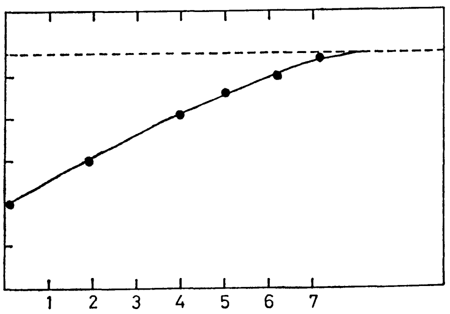

Fig. 6. The time dependence of the photoemission for the H_2-exposed benzonitrile-cesium complex under pumping. I_0 is the value of quantum yield for the fresh film.

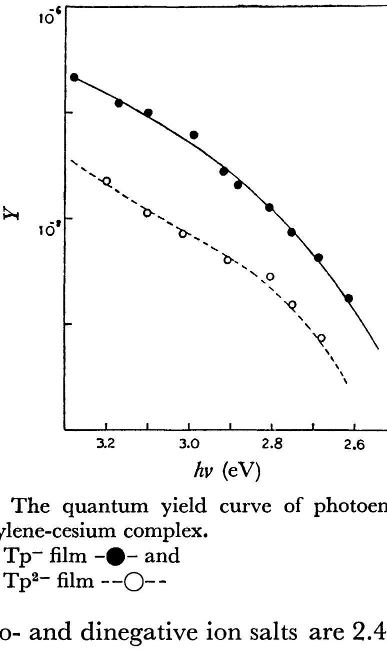

Fig. 7. The quantum yield curve of photoemission for triphenylene-cesium complex.
for Tp^- film -●- and
for Tp^{2-} film --○--

Some aromatic-alkali metal ion radical salts have been found to have a good catalytic activity for hydrogen-deuterium equilibration, $H_2+D_2=2HD$; this catalytic activity may arise from the excess charge, which participates in forming the chemisorotion bond with H_2 on the ion-radical salt in the solid phase.[15] This proposal is supported by these photoemission results.

On the other hand, we have already reported that the distinction of the valencies on the anion produces a large difference in their catalytic acitvity; the reaction rate for the dinegative ion salt was found to be ten times that of the mononegative ion salt at room temperature.[5,15,16] Although no quantitative correlation between the catalytic acitvity and the photoemissive character as functions of the valencies of the anion can be found, we

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[11] M. Kochi, Y. Harada, T. Hirooka, and H. Inokuchi, This Bulletin, **43**, 2690 (1970).

[12] H. Inokuchi, N. Wakayama, and T. Hirooka, *J. Catal.*, **8**, 383 (1967).

[13] The value corresponds to ΔE, the energy difference between the E_{th} values of the fresh sample and the H_2-exposed one.

[14] During this experiment, the photoemission was measured with a 220-mμ incident light.

[15] T. Kondow, H. Inokuchi, and N. Wakayama, *J. Chem. Phys.*, **43**, 3766 (1965); H. Inokuchi, *Discuss. Faraday Soc.*, **51**, 183 (1971).

[16] N. Wakayama, Y. Mori, and H. Inokuchi, *J. Catal.*, **12**, 15 (1968).

now intend to make further studies of the behaviour of the excess charge in ion-radical salts.

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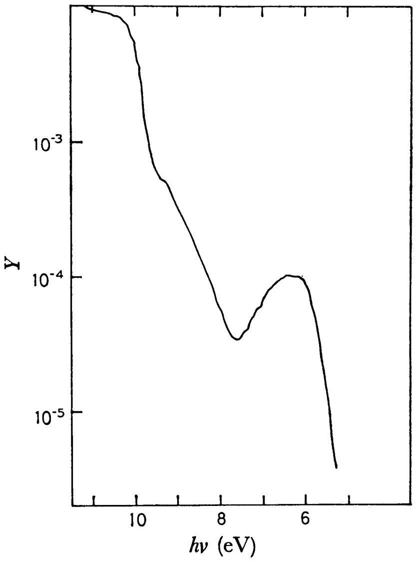

Fig. 8. The spectral response curve of the photoemissive quantum yield for triphenylene-cesium salt in the vacuum ultraviolet region.

Appendix

The photoemission from the benzonitrile-Cs complex was measured in the vacuum-ultraviolet region. Figure 8 shows the spectral response curve of the photoemissive quantum yield. In the curve, a sharp minimum at the photon energy of 7.65 eV was found. The minimum may be the emission from the second-highest occupied level of the benzonitrile anion. This assumption is supported by the fact that the difference (7.65−5.11=2.54 eV) between the minimum (7.65 eV) and the threshold value (5.11 eV) agrees with the absorption peak of the anion, 490 mμ (2.54 eV), and corresponds to the transition between the highest occupied level and the second highest occupied level, as is shown in the following diagram.