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# Light-induced Electron Emission from Polymethylphenyl Siloxane Oils

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## ABSTRACT

Light-induced electron emission from tetramethyl tetraphenyl trisiloxane, (Dow-Corning silicone oil DC704) and trimethyl pentaphenyl siloxane (Wacker Chemie silicone oil AN175) has been measured as a function of photon energy. Absolute quantum yield and threshold energy were determined. The threshold energy of 7.5 eV for both siloxanes is comparable to the thresholds of other polymethylphenyl siloxanes with phenyl/methyl ratios of 1/3 and 1/18, which were already investigated by the authors. The quantum yield as a function of photon energy shows a systematic change with variation of the phenyl/methyl ratio. This dependence on the molecular structure is ascribed to a change of the initial ionization quantum yield.

## 1. INTRODUCTION

SILICONE oils have been used as liquid insulators and coolants in transformers because of their high flash point and their excellent dielectric properties. Many studies on the electrical conductivity of these oils have been published [1-5]. However, the various factors influencing the insulating state are not well understood. Further information on their electronic properties is an important prerequisite for improvement of their application. Measurements of photoconductivity and light-induced electron emission are powerful tools for the study of the energetics of charge carrier generation. The photoconductivity threshold  $E_{th}(pc)$  in the liquid is shifted with respect to its vacuum value  $E_{th}(gas)$ , due to the polarization energy  $P_+$  of the cation, the electron affinity of the liquid  $V_0$ , and the broadening of the valence levels due to condensation  $E_{val}$ .

$$E_{th}(pc) = E_{th}(gas) + P_+ + V_0 + E_{val} \quad (1)$$

While  $P_+$  is always negative,  $V_0$  may be either positive or negative.  $E_{val}$  is of the order of 0.1 eV. In light-induced electron emission experiments the threshold energy for emission in vacuo,  $E_{th}(vac)$ , is governed by the following relation,

$$E_{th}(vac) = E_{th}(gas) + P_+ + E_{val} \quad (2)$$

Both techniques combined actually can be used to determine  $V_0$ . Baron *et al.* [6] measured the VUV photoconductivity of some silicone oils. We studied the light-induced electron emission from these oils [7, 8]. The threshold energies of photoconductivity and photoelectron emission of the polymethylphenyl siloxane oils (PMPS) were found to be lower than those of the polydimethyl siloxane oils (PDMS). The threshold energy of PMPS

( $E_{th} \approx 7.65$  eV) is determined by the  $\pi$  electrons of phenyl groups, while that of PDMS ( $E_{th} \approx 8.35$  eV) is determined by  $\sigma$  electrons. The difference in the thresholds of PMPS and PDMS is ascribed to the different binding energies of  $\pi$  and  $\sigma$  electrons [7, 9, 10]. Within experimental error, the threshold and the absolute quantum yield were found to be independent of the chain length of the molecule. However, for the PMPS, the phenyl/methyl ratios influenced the quantum yield.

The purpose of this paper is to elucidate the dependence of the quantum yield on the phenyl/methyl ratio. We measured the photoelectron emission from tetramethyl tetraphenyl trisiloxane (Dow-Corning silicone oil DC704) and trimethyl pentaphenyl siloxane which are PMPS with a higher phenyl/methyl ratio than the silicone oils (AP100, AS100 of Wacker Chemie) which we measured previously [8].

## 2. EXPERIMENTAL

The experimental setup was described previously [7, 8]. A thin liquid film was put on the cathode. Vacuum ultraviolet light from a deuterium discharge lamp was monochromatized by a vacuum monochromator and fell on the cathode through an anode mesh. Current induced by photoelectron emission was measured as a function of photon energy. The relative light intensity was monitored by the fluorescence of sodium salicylate [11]. Division of the current by the intensity of the fluorescence gave the relative photoelectron emission yield. The absolute quantum yield was obtained from the measurement of the photoemission current of a thin gold film, the absolute quantum yield of which was reported by Cairns and Samson [12].

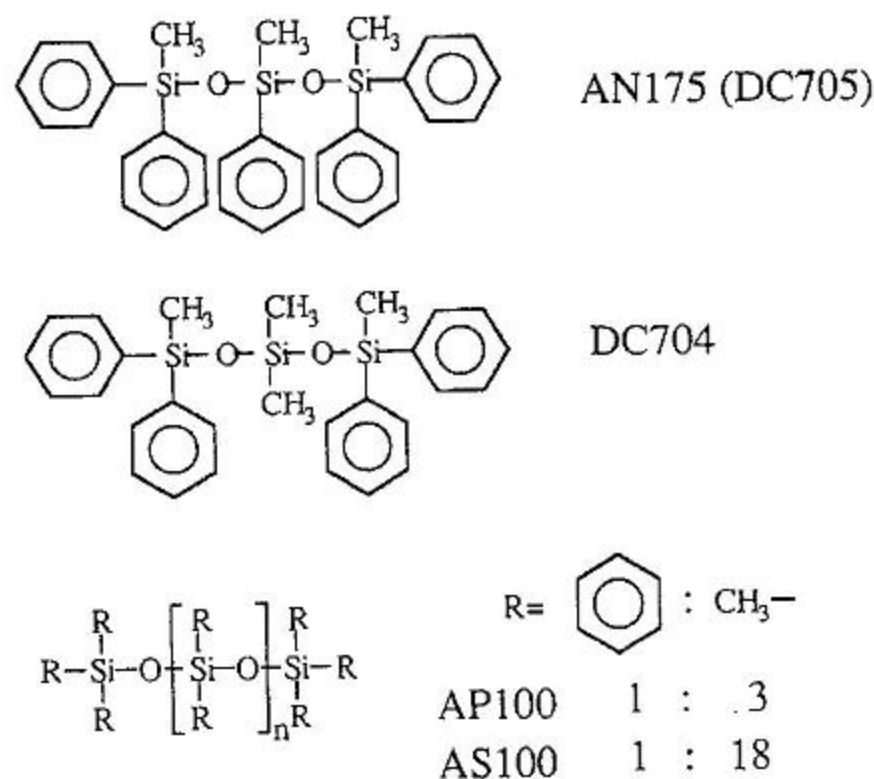


Figure 1. Structure of silicone oils.

The silicone fluids studied are tetramethyl tetraphenyl trisiloxane, (Dow Corning silicone oil DC704) and trimethyl pentaphenyl siloxane (Wacker Chemie silicone oil AN175). Wacker's AN175 is equivalent to Dow Corning's DC705. The fluids were used as received. The chemical structures of the PMPS oils are shown in Figure 1.

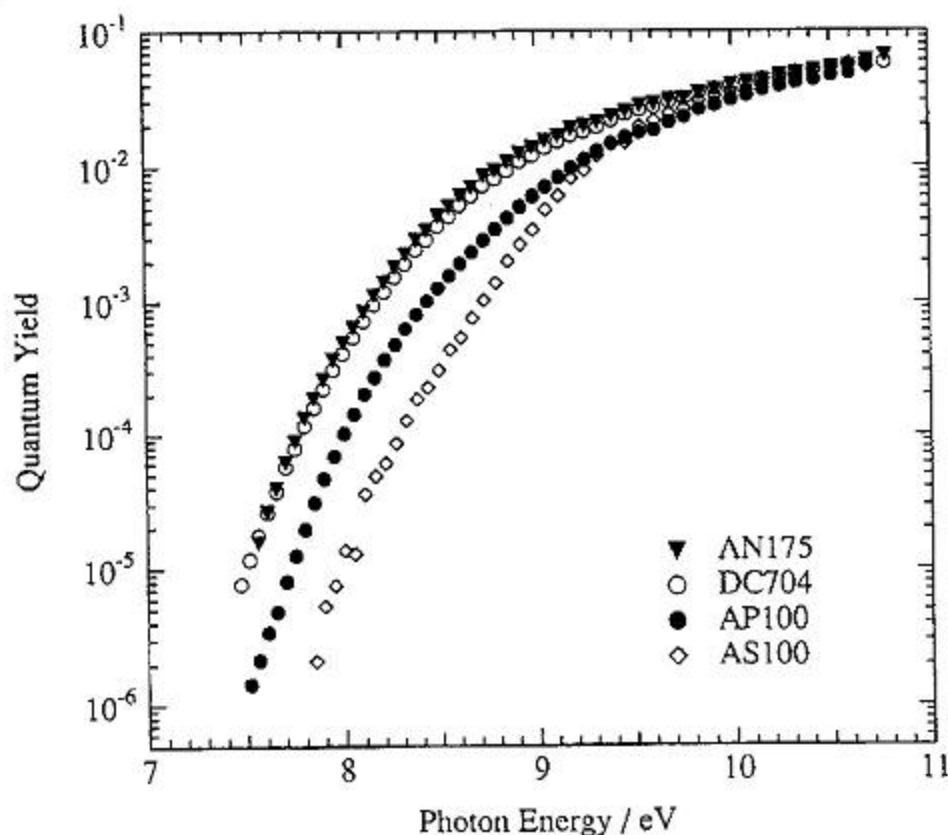


Figure 2. Photo electron emission quantum yields for silicone oils: AN175, DC704, AP100, and AS100.

### 3. RESULTS

Figure 2 shows the quantum yield curve of photoelectron emission for DC704 and AN175. The curves for AP100 and AS100 are included. The quantum yield increases with increasing the ratio at low photon energies. above 10 eV these differences disappear. The threshold energy was determined by applying a power law [13, 14],

$$Y = (h\nu - E_{th})^3 \quad (3)$$

As shown in Figure 3, the photoelectron emission threshold is determined to be  $E_{th} = 7.5 \pm 0.2$  eV for DC704 and AN175. The

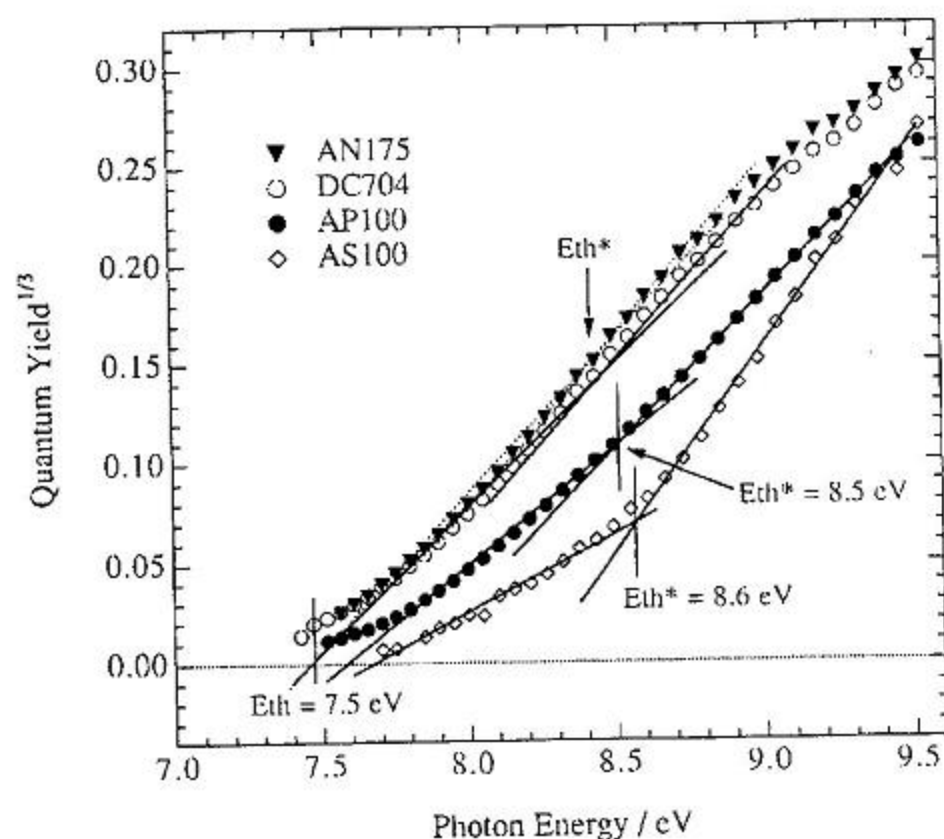
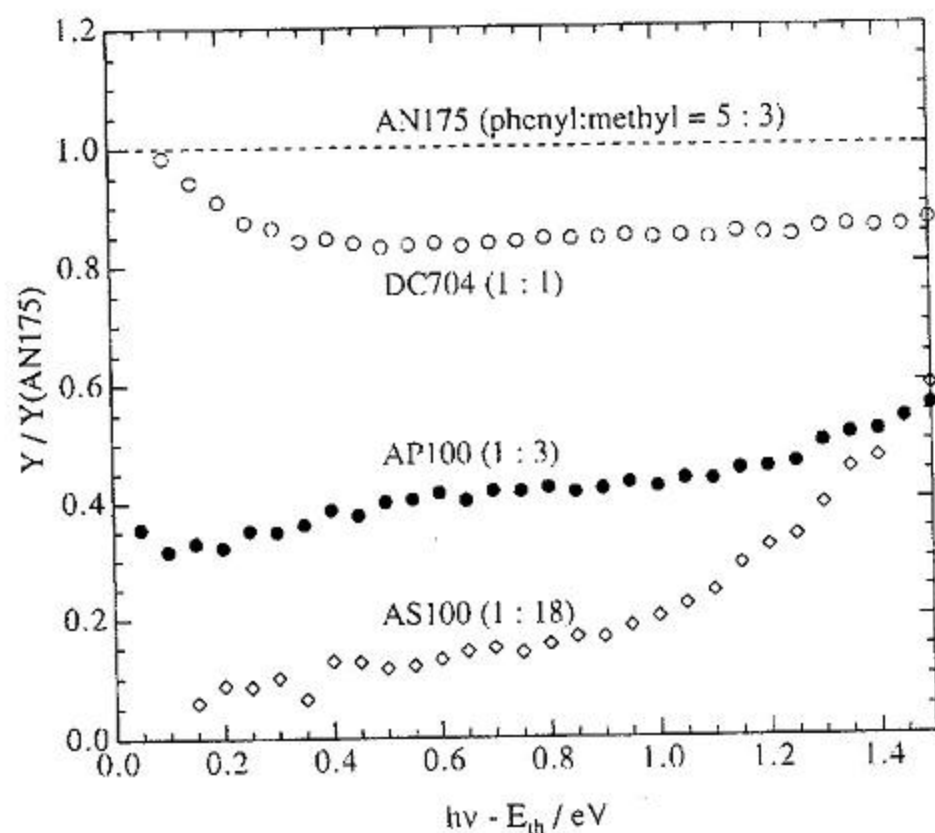


Figure 3. Quantum yields near the threshold region plotted as the power function given by Equation (1).

Figure 4. Ratio of photo-electron emission yields of DC740, AP100, and AS100 to the yield of AN175 plotted as a function of excess energy ( $h\nu - E_{th}$ ).

onset of another component is observed at 8.5 and 8.6 eV ( $E_{th}^*$ ) in AP and AS, respectively. This is due to the ionization of lone-pair electrons of the oxygen atom or of  $\sigma$  electrons of Si-C, Si-O or C-H bonds. This threshold is only slightly indicated in DC704 and AN175 with the higher phenyl/methyl ratio. In Figure 4, relative emission yields are plotted against the excess energy. They increase with increasing the phenyl/methyl ratio.

### 4. DISCUSSION

Photoelectron emission involves several processes: absorption of a photon, ionization of a molecule, electron transport to the liquid/vacuum interface and escape into the vacuum. An incident photon is absorbed by a molecule of the liquid at a distance between  $x$  and  $x + dx$  from the surface with a probability of  $\mu \exp(-\mu x) dx$ , where  $\mu$  is the photoabsorption coefficient.

The molecule which absorbed a photon ionizes with an ionization quantum yield  $\eta$ . The ejected electron travels in the liquid losing its excess energy with elastic and inelastic collisions becoming thermalized, eventually. If the electron has still enough kinetic energy when it reaches the surface to overcome the barrier given by  $V_0$ , the electron is emitted into the vacuum. Koizumi derived an equation relating the photoelectron emission yield  $\eta$  to  $\mu$ , and the distribution function of thermalized geminate charge carrier pairs,  $F(b, r)$  [10].  $b$  is the average thermalization distance, and  $r$  is the separation distance of geminate pairs. Assuming an exponential function

$$F(r, b) = \frac{1}{b} \exp\left[-\frac{r}{b}\right] \quad (4)$$

the quantum yield  $Y$  of photoelectron emission is then calculated to be

$$Y = \frac{1}{2}\eta \left[1 - \frac{1}{\mu b} \ln(1 + \mu b)\right] \quad (5)$$

The value of  $Y$  is determined by the three quantities,  $\eta$ ,  $\mu$ , and  $b$ . It increases with increasing  $\eta$ ,  $\mu$  and  $b$ . The dependence of the photoelectron emission yield on the phenyl/methyl ratio may then be due to an alteration of these three quantities with the changing of the chemical structure of the silicone oils.

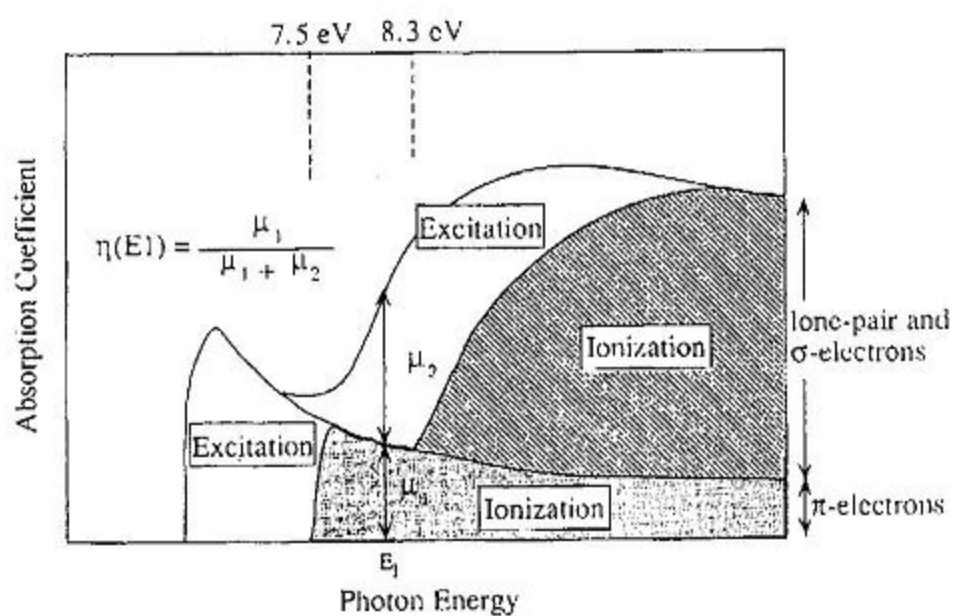


Figure 5. Schematic representation of the correlation between absorption coefficient  $\mu$  and excitation and ionization of polymethylphenyl siloxane oils. The coefficient is divided into two components: the component  $\mu_1$  due to  $\pi$  electrons and the component  $\mu_2$  due to lone-pair and  $\sigma$  electrons. If the excitation of lone-pair and  $\sigma$  electrons causes no ionization below their ionization threshold of 8.3 eV, the initial quantum yield of photoionization ( $\eta$ ) between 7.5 eV and 8.3 eV is given as  $\eta(E_1) = \mu_1 / (\mu_1 + \mu_2)$ .

We assume that the dependence of  $Y$  on the phenyl/methyl ratio is due to differences in  $\eta$ . Figure 5 shows a schematic diagram of the absorption coefficients of PMPS. The ionization of the  $\pi$  electrons starts at  $\sim 7.5$  eV, and that of the lone pair electrons and the  $\sigma$  electrons starts at  $\sim 8.3$  eV. Absorption due to electronic excitation starts several eV below the ionization threshold [15]. Between 7.5 and 8.3 eV, a photon causes ionization of a  $\pi$  electron or excitation of a  $\sigma$  electron. If we assume that the latter excitation does not cause ionization, in other words, if these excited states do not autoionize, we can explain the dependence of

Table 1. Quantum yield of photoelectron emission ( $Y$ ) at an excess energy of  $(h\nu - E_{th}) = 0.5$  eV and concentration of phenyl groups of the polymethylphenyl siloxane oils.

Compound phenyl:methyl	Quantum yield		Phenyl groups	
	abs.	rel.	conc. $10^{21} \text{ cm}^{-3}$	rel.
AN175 (5:3)	$5.0 \times 10^{-4}$	1.0	6.0	1.0
DC704 (1:1)	$4.1 \times 10^{-4}$	0.82	5.3	0.89
AP100 (1:3)	$2.0 \times 10^{-4}$	0.40	3.1 to 3.6 <sup>a</sup>	0.51 to 0.60 <sup>a</sup>
AS100 (1:18)	$6.1 \times 10^{-5}$	0.12	7.9 to 8.1 <sup>b</sup>	0.13 to 0.14 <sup>b</sup>

(a) Calculated for the structure of Figure 1 with  $n = 1$  to 99.  
(b) Calculated for the structure of figure 1 with  $n = 16$  to 92.

the quantum yields on phenyl/methyl ratio. The initial ionization quantum yield  $\eta$  is defined by

$$\eta = \frac{\text{ions produced}}{\text{photons absorbed}} \quad (6)$$

With the above assumption, the ionization is due to the  $\pi$  electrons of the phenyl groups and the absorption is due to the  $\pi$  and  $\sigma$  electrons in this region. The number ratio of  $\pi$  electrons to the sum of  $\pi$  and  $\sigma$  electrons increases with increasing phenyl/methyl ratio. Hence,  $\eta$  increases with increasing the phenyl/methyl ratio. In the region  $> 8.3$  eV,  $\sigma$  electrons contribute to ionization, in addition. The value of  $\eta$  levels off.

The thermalization distance  $b$  depends on the phenyl/methyl ratio in a different way.  $b$  values of 6.1 to 6.5 nm for PDMS irradiated with ionizing radiation were reported by Schmidt and Holroyd [16]. Although thermalization distances for PMPS have not been reported yet, data for various liquid aromatics [17] and alkanes [18] show that the  $b$  values for aromatics are smaller than those of the corresponding alkanes. Replacement of methyl groups by phenyl groups will decrease  $b$ . Hence,  $Y$  for PMPS should decrease with increasing phenyl/methyl ratio contrary to our finding.

An increase of the absorption coefficient  $\mu$  would also affect the value of  $Y$  due to the fact that the attenuation length of the light would become shorter thus making it easier for the ionized electrons to escape into the vapor space. Measurements of  $\mu$  by Baron *et al.* and Sowers *et al.* do not show a large difference at 8 eV between PDMS and PMPS oils [19, 6]. On the other hand, the quantum yield at 0.5 eV above the threshold correlates nicely with the concentration of phenyl groups (see Table 1). This may serve as an indication that the ionization in this energy range is due to ionization of phenyl groups.

## 5. CONCLUSION

THE increase of the photoelectron emission quantum yield with increasing phenyl/methyl ratio is ascribed to the change of the initial photoionization quantum yield due to an increase of concentration of phenyl groups. This indicates that states formed from the excitation of a  $\sigma$  or lone pair electron, so-called superexcited states [20], have a low probability of autoionization. They

will dissociate predominantly into neutral products as is the case for superexcited organic molecules in the gas phase [21].

## REFERENCES

- [1] R. M. Hakim, R. G. Olivier, and H. St-Onge, "The Dielectric Properties of Silicone Fluids", *IEEE Trans. Electr. Insul.*, Vol. 12, pp. 360–370, 1977.
- [2] S. Yasufuku, T. Umemura, and Y. Ishioka, "Phenyl-methyl-silicone Fluid and its Application to HV Stationary Apparatus", *IEEE Trans. Electr. Insul.*, Vol. 12, pp. 402–410, 1977.
- [3] J. G. Rabe, W. F. Schmidt and W. J. Klein, "Physico-chemical Investigation of the Behavior of Silicone Oils under the Influence of High-voltage Stress", *Electrostatics*, Vol. 7, pp. 253–266, 1979.
- [4] H. Shimokawa, A. Ohashi and M. Ueda, "Conduction Currents in Silicone Liquid Films", *J. Electrostatics*, Vol. 7, pp. 187–197, 1979.
- [5] H. Shimokawa, A. Ohashi and M. Ueda, "High Field Conduction in Dielectric Liquid Films in the Time Range  $10^{-5}$  to  $10^{-3}$  s", *J. Electrostatics*, Vol. 12, pp. 179–187, 1982.
- [6] P. L. Baron, J. Casanovas, J. P. Guelfucci and L. S. Hoi, "Photoconductivity Induced by VUV Photons in Polydimethyl siloxane and Polymethylphenyl siloxane Oils", *IEEE Trans. Electr. Insul.*, Vol. 23, pp. 563–570, 1988.
- [7] H. Koizumi, K. Lacmann and W. F. Schmidt, "Light-induced Electron Emission from Silicone Oils", *J. Phys. D: Appl. Phys.*, Vol. 25, pp. 857–861, 1992.
- [8] H. Koizumi, K. Lacmann and W. F. Schmidt, "VUV Light-induced Electron Emission from Organic Liquids", *J. Electron Spectrosc. Rel. Phenom.*, Vol. 67, pp. 417–427, 1994.
- [9] T. Sugano, K. Seki, T. Ohta, H. Fujimoto and H. Inokuchi, "UV Photoelectron Study of the Electronic Structure of Poly (Dimethylsiloxane) and the Comparison with Related Silicon Compounds", *Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.)*, pp. 594–598, 1990.
- [10] H. Koizumi, "Photoionization Quantum Yield for Squalane and Squalene Estimated from Photoelectron Emission Yield", *Chem. Phys. Lett.*, Vol. 219, pp. 137–142, 1994.
- [11] J. A. R. Samson, *Techniques of Vacuum Ultraviolet Spectroscopy*, Wiley, New York, 1967.
- [12] R. B. Cairns and J. A. R. Samson, "Metal Photocathodes as Secondary Standards for Absolute Intensity Measurements in the Vacuum Ultraviolet", *J. Opt. Soc. Am.*, Vol. 56, pp. 1568–1573, 1966.
- [13] M. Kochi, Y. Harada, T. Hirooka and H. Inokuchi, "Photoemission from Organic Crystal in Vacuum Ultraviolet Region IV", *Bull. Chem. Soc. Japan*, Vol. 43, pp. 2690–2702, 1970.
- [14] A. I. Belkind, A. M. Brodskii and V. V. Grechov, "Theory of Photoemission from Molecular Crystals", *Phys. Stat. Sol. B.*, Vol. 85, pp. 465–472, 1978.
- [15] M. B. Robin, *Higher Excited States of Polyatomic Molecules*, Vol. 1, Academic Press, New York, 1974.
- [16] W. F. Schmidt and R. A. Holroyd, "Ion Mobilities and Yields in X-irradiated Polydimethyl siloxane Oils", *Radiat. Phys. Chem.*, Vol. 39, pp. 349–353, 1992.
- [17] K. Shinsaka and G. R. Freeman, "Epithermal Electron Ranges and Thermal Electron Mobilities in Liquid Aromatic Hydrocarbons", *Can. J. Chem.*, Vol. 52, pp. 3495–3506, 1974.
- [18] G. R. Freeman, "Ionization and charge separation in irradiated materials", in *Kinetics of Nonhomogeneous Processes*, (Hrsg.: G. R. Freeman) Wiley, New York, 1987.
- [19] B. L. Sowers, M. W. Williams, R. N. Hamm and E. T. Arakawa, "Optical Properties of Some Silicone Diffusion-pump Oils in the Vacuum Ultraviolet - Using a Closed-cell Technique", *J. Appl. Phys.*, Vol. 42, pp. 4252–4257, 1971.
- [20] R. L. Platzman, "Superexcited States of Molecules, and the Primary Action of Ionizing Radiation", *Vortex.*, Vol. 23, pp. 372–389, 1962.
- [21] H. Koizumi, "Predominant Decay Channel for Superexcited Organic Molecules", *J. Chem. Phys.*, Vol. 95, pp. 5846–5852, 1991.

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