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The Mechanism of the Forming of Cooper Pairs in Aromatic Hydrocarbons

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Abstract

The experimental results for the photoemission energy of Cooper pairs from aromatic hydrocarbons such as benzene (**6an**), naphthalene (**10ac**), and anthracene (**14ac**), recently reported, are rationalized. We can rationalize these results by considering that the electron Cooper pairs in the microscopic sized molecules such as **6an**, **10ac**, and **14ac** can be formed by the stable spin singlet states as a consequence of large energy gaps between the occupied and unoccupied orbitals formed by quantization of the orbitals, and by large negative Coulomb interactions between two electrons occupying the same orbitals via the positively charged nuclei. Observation of large photoemission energy of Cooper pairs of about 70~80 eV, similar to the attractive Coulomb energies between two electrons of a Cooper pair, means that the existence of a bosonic particle with zero kinetic energy (i.e., Cooper pair), as predicted in our previous researches, can be confirmed.

Keywords: Photoemission of Bosonic Cooper Pairs; Fermionic Two Electrons; Attractive Coulomb Interactions between Two Electrons; Zero Kinetic Energy

1. Introduction

The effect of vibronic interactions and electron–phonon interactions [1–8] in molecules and crystals is an important topic of discussion in the modern physics. The vibronic and electron–phonon interactions play an essential role in various research fields such as the distortion of molecular structures, Jahn–Teller effects, Peierls distortions, spectroscopy, electrical conductivity, and superconductivity [1–8]. We have investigated the electron–phonon interactions in various charged molecular crystals for more than ten years [1–8]. In particular, in 2002, we predicted the occurrence of superconductivity as a consequence of vibronic interactions in the negatively charged picene, anthracene, and coronene [8]. Recently, it was reported that these trianionic molecular crystals exhibit superconductivity [9].

The application of molecular orbital theory to the magnetic properties was developed by London in 1937 [1–8,10]. Pople developed the modified secular equations in the presence of an external magnetic field, in particular, the important magnetic property of aromatic molecules associated to the existence of ring currents [1–8,10]. The diamagnetic anisotropy of aromatic hydrocarbons such as polyacenes (benzene (**6an**), naphthalene (**10ac**), anthracene (**14ac**), and tetracene (**18ac**)) can be attributed to the induced ring currents in their π-electronic systems [11–14]. The diamagnetic ring currents of aromatic molecules such as polyacenes are nondissipative diamagnetic currents similar in many respects to the persistent currents of superconducting rings and have been referred to as a form of superconductivity [11–14]. However, the mechanism of the occurrence of the nondissipative diamagnetic currents in the microscopic sized molecules has not been elucidated for more than 70 years.

In the previous works [1–8,11–14], we suggested the mechanism of the occurrence of the nondissipative diamagnetic currents in the microscopic sized polyacene molecules such as **6an**, **10ac**, **14ac**, and **18ac**. Furthermore, we suggested the unified theory by which the mechanism of the occurrence of the supercurrents in the macroscopic sized conventional superconductivity as well as in the microscopic sized molecules such as **6an**, **10ac**, **14ac**, and **18ac** can be explained. According to the previous researches [1–8,11–14], the electron Cooper pairs in the microscopic sized molecules such as **6an**, **10ac**, **14ac**, and **18ac** can be formed by the closed-shell electronic structures with large energy gaps between the occupied and unoccupied orbitals formed by quantization of the orbitals by nature, and large negative Coulomb interactions between two electrons with opposite momentum and spins occupying the same orbitals via the positively charged nuclei. On the other hand, according to the previous researches [1–8,11–14], the electron Cooper pairs in the macroscopic sized conventional superconductivity can be formed by the closed-shell electronic structures with small energy gaps between the occupied and unoccupied orbitals formed by electron–phonon interactions and large negative Coulomb interactions between two electrons.

A photon of sufficient energy can interact with a single electron that is bound in an atom or molecule leading to photoemission of that electron leaving behind a singly charged ion. However, due to electron correlation the emissions of two electrons by a single photon, called double photoionization, is also possible. Many

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investigations of the double-photoionization process using different techniques have been performed on atoms over several years [15,16]. A recent double-photoionization experiment on polyacenes [15] found that the ratio of doubly to singly charged parent ions increases with an increase in the molecular size and that the double-photoionization process is dominated by the same mechanism as for atoms for energies up to about 30 eV above the threshold. Furthermore, recently, Wehlitz et al. reported the discovery of the photoemission of Cooper pair in **6an**, **10ac**, **14ac**, and coronene [16].

In this article, we will try to rationalize the experimental results for the photoemission of Cooper pairs from aromatic hydrocarbons, reported by Wehlitz et al. [16], on the basis of the hypotheses suggested in the previous researches [1–8,11–14], as described above.

2. The Mechanism of the Forming of Electron Cooper Pairs in the Microscopic Sized Molecules

Let us look into the mechanism of the forming of electron Cooper pairs in the microscopic sized molecules. The electronic structures in the microscopic sized molecules and in the macroscopic sized conventional superconductivity are shown in Fig. 1 (a). In our previous researches [1–8,11–14], we suggested that the Coulomb interactions between two electrons with opposite momentum and spins occupying the same orbitals become attractive via the existence of the Coulomb interactions between all nuclei and electrons. Furthermore, the stable spin singlet electronic states of two electrons with opposite momentum and spins are formed by large HOMO–LUMO gaps ($\Delta E_{\mathrm{HOMO-LUMO}}$) as a consequence of the quantization of orbitals formed by nature. That is, because of large attractive Coulomb interactions between all nuclei and electrons, and large HOMO–LUMO gaps as a consequence of the quantization of orbitals formed by nature, two electrons with attractive Coulomb interactions and the stable spin singlet states are in the bound states. Therefore, electron Cooper pairs can be formed.

The total Coulomb interactions for the orbital j occupied by an electron with spin σ in N carrier states ($V_{\mathrm{Coulomb,total},N}\left(\boldsymbol{k}_j\sigma\right)$) are caused by the Coulomb interactions between electrons ($V_{\mathrm{Coulomb,e-e},N}\left(\boldsymbol{k}_j\sigma\right)>0$), between electrons and nuclei ($V_{\mathrm{Coulomb,e-n},N}\left(\boldsymbol{k}_j\sigma\right)<0$), and between nuclei ($V_{\mathrm{Coulomb,n-n},N}\left(\boldsymbol{k}_j\sigma\right)>0$). Therefore, the total Coulomb energies can be defined as,

$$V_{\mathrm{Coulomb,total},N}\left(\boldsymbol{k}_j\sigma\right)=V_{\mathrm{Coulomb,e-e},N}\left(\boldsymbol{k}_j\sigma\right)+V_{\mathrm{Coulomb,e-n},N}\left(\boldsymbol{k}_j\sigma\right)+V_{\mathrm{Coulomb,n-n},N}\left(\boldsymbol{k}_j\sigma\right) \quad (1)$$

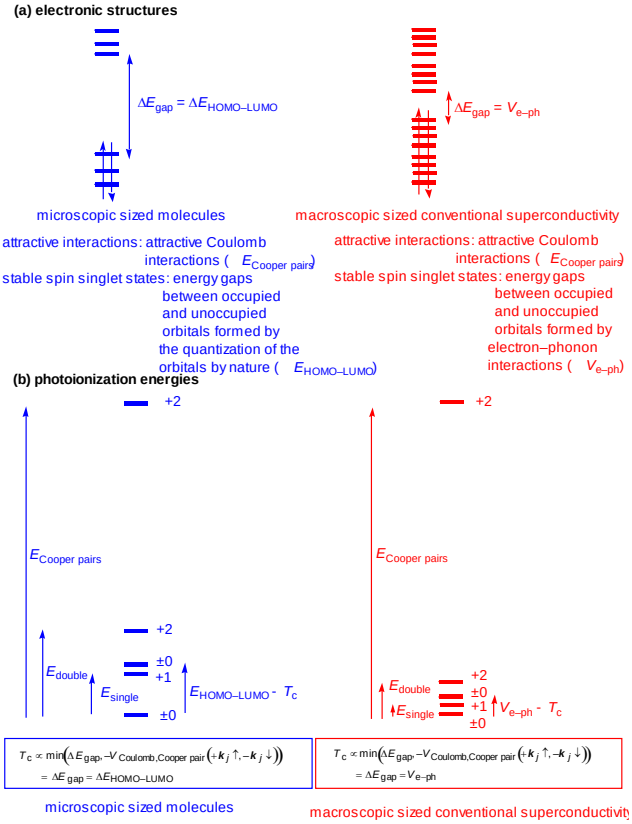

Fig. 1. (a) Electronic structures in the microscopic sized molecules and in the macroscopic sized conventional superconductivity. (b) Energy diagram for the photoionizations in the microscopic sized molecules and in the macroscopic sized conventional superconductivity.

Orbital energies for the orbital j with spin σ in N carrier states ($\varepsilon_N\left(\boldsymbol{k}_j\sigma\right)$) can be estimated as follows,

$$\varepsilon_N\left(\boldsymbol{k}_j\sigma\right)=V_{\mathrm{kin},N}\left(\boldsymbol{k}_j\sigma\right)+V_{\mathrm{Coulomb},N}\left(\boldsymbol{k}_j\sigma\right), \quad (2)$$

where the $V_{\mathrm{kin},N}\left(\boldsymbol{k}_j\sigma\right)$ is the kinetic energy of an electron with spin σ occupying the orbital j in materials with N carriers. From this equation, the $V_{\mathrm{Coulomb},N}\left(\boldsymbol{k}_j\sigma\right)$ value can be estimated as,

$$V_{\mathrm{Coulomb},N}\left(\boldsymbol{k}_j\sigma\right)=\varepsilon_N\left(\boldsymbol{k}_j\sigma\right)-V_{\mathrm{kin},N}\left(\boldsymbol{k}_j\sigma\right) \quad (3)$$

Since the $V_{\mathrm{kin},N}\left(\boldsymbol{k}_j\sigma\right)$ values are always large positive and the $\varepsilon_N\left(\boldsymbol{k}_j\sigma\right)$ values for the occupied orbitals are

usually negative or very small positive, the $V_{\text{Coulomb},N}(\boldsymbol{k}_j\sigma)$ values for the occupied orbitals usually become very large negative even in charged materials [1–8,11–14]. As listed in Fig. 2 and Table 1, the $\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values are estimated to be –6.702, –5.787, and –5.225 eV, the $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values are estimated to be 30.435, 32.217, and 33.345 eV, the $V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values are estimated to be –37.137, –38.004, and –38.570 eV, and the $\Delta E_{\text{HOMO–LUMO}}$ values are estimated to be 9.22, 7.97, and 6.93 eV in **6an**, **10ac**, and **14ac**, respectively, by using the hybrid Hartree–Fock (HF)/density-functional-theory (DFT) method of Becke [17], and Lee, Yang, and Parr [18] (B3LYP) and the 6-31G* basis set [19,20], as in our previous studies [1–8,11–14]. The Gaussian 03 program package [21] was used for our theoretical analyses.

Table 1. The estimated $\Delta E_{\text{HOMO–LUMO}}$, $\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$, $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$, $V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$, E_{double} (Ref. [15]), $V_{\text{Coulomb,Cooper pair}}(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow)$, $V_{\text{kin,Cooper pair}}(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow)$, and $E_{\text{Cooper pair}}$ (Ref. [16]) values (in eV).

	$\Delta E_{\text{HOMO–LUMO}}$	$\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$
6an	9.22	–6.702
10ac	7.97	–5.787
14ac	6.39	–5.225

$V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$	$V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$	E_{double} (exp.)
30.435	–37.137	24.927
32.217	–38.004	21.391
33.345	–38.570	20.072

$V_{\text{kin,Cooper pair}}(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow)$
0.000
0.000
0.000

$E_{\text{Cooper pair}}$ (exp.)
51.213
51.867
54.358

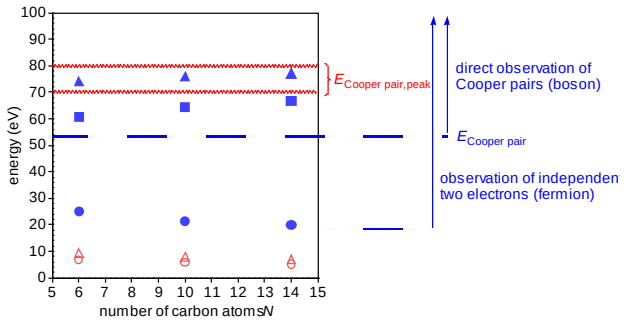

Fig. 2. Various energies versus the molecular size. The opened circles and triangles denote the $-\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$ and $\Delta E_{\text{HOMO–LUMO}}$ values, respectively. The closed circles, triangles, and squares denote the E_{double}, $-V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma')$, and $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma')$ values, respectively.

3. Photoionization

Let us look into the photoionization in the neutral **6an**, **10ac**, and **14ac**. We define the thresholds for the single-photoionization as E_{single}, for the double-photoionization as E_{double}, and for the Cooper pair photoionization as $E_{\text{Cooper pair}}$. Furthermore, we define the energy for the peak of the ratio of the occurrence of the direct destruction of the Cooper pair as $E_{\text{Cooper pair,peak}}$ [16].

3.1 Below Single-Photoionization Threshold

According to the previous researches [1–8,11–14], there can be electron Cooper pairs and nondissipative diamagnetic supercurrents at room temperatures in the microscopic sized molecules such as the neutral **6an**, **10ac**, and **14ac**. The thresholds for the single photoionization (E_{single}) can be defined as

$$E_{\text{single}} \approx -\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma) = -V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma) - V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma), \quad (4)$$

where the $\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$ value is the energy level of the highest occupied molecular orbitals (HOMO), the $V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$ value denotes the Coulomb interactions between an electron occupying the HOMO and another electrons and nuclei, and the $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$ value is the kinetic energy for an electron occupying the HOMO with spin σ.

When energy of a photon (E_{photon}) is smaller than the E_{single} value, that is, at $E_{\text{photon}} < E_{\text{single}}$, a photon cannot be absorbed by any electron, as shown in Figs. 3 (a) and 4 (a), and thus the Cooper pair and the nondissipative diamagnetic supercurrents cannot be destroyed. This is

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because any excited energy level of electronic state which is higher than the superconducting ground states, does not exist below the E_{single} value with respect to the superconducting ground state, as shown in Fig. 1 (b).

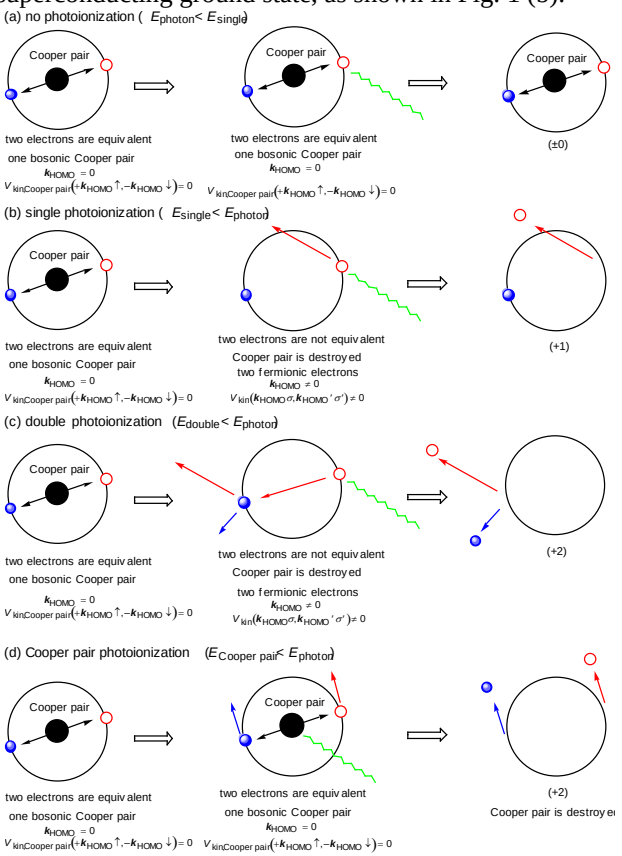

Fig. 3. The sketch of the various photoionizations mechanism. The shaded and opened circles indicate the electrons moving around the molecule, clockwise and counter-clockwise, respectively. (a) No photoionization ($E_{\text{photon}} < E_{\text{single}}$). (b) Single photoionization ($E_{\text{single}} < E_{\text{photon}}$). (c) Double photoionization ($E_{\text{double}} < E_{\text{photon}}$). (d) Cooper pair photoionization ($E_{\text{Cooper pair}} < E_{\text{photon}}$).

3.2 Single-Photoionization Processes

Let us next consider the single-photoionization processes. The E_{single} values are considered to be similar to the $-\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values. The $\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values are estimated at the B3LYP/6-31G* level to be –6.702, –5.787, and –5.225 eV, respectively. At $E_{\text{single}} < E_{\text{photon}} < E_{\text{double}}$, a photon can be absorbed by one of two electrons, as shown in Figs. 3 (b) and 4 (b). Even though it is very difficult for the bosonic electron Cooper pairs formed by strong Coulomb interactions between equivalent two fermionic electrons to be directly

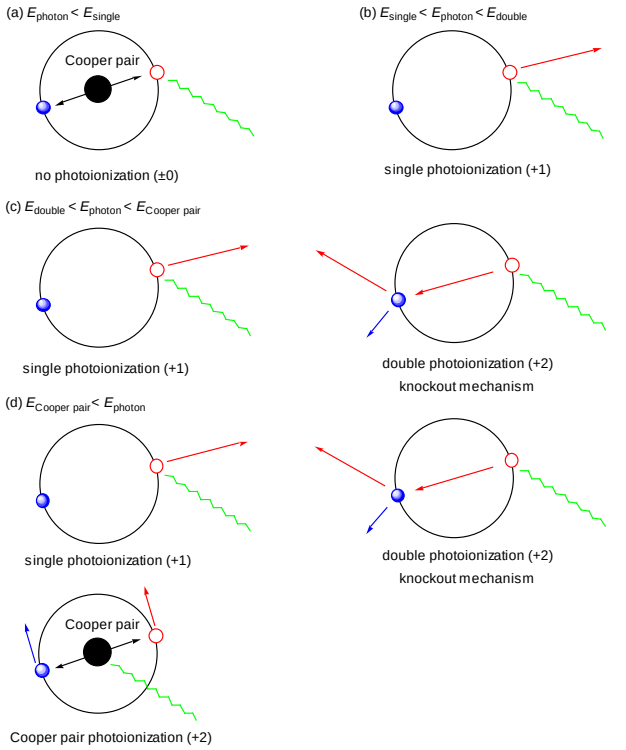

Fig. 4. Various photoionizations as a function of the energy of a photon. The shaded and opened circles indicate the electrons moving around the molecule, clockwise and counter-clockwise, respectively. (a) $E_{\text{photon}} < E_{\text{single}}$. (b) $E_{\text{single}} < E_{\text{photon}} < E_{\text{double}}$. (c) $E_{\text{double}} < E_{\text{photon}} < E_{\text{Cooper pair}}$. (d) $E_{\text{Cooper pair}} < E_{\text{photon}}$.

destroyed, if a photon with the energies higher than the E_{single} value is absorbed by one of two electrons occupying the HOMO, such one of two electrons is emitted and removed from the molecule and the electronic states in the molecule are in the excited monocationic states. In such a case, an electron absorbing a photon and emitted from the molecule is not equivalent to another electron anymore, and thus these electrons independently behave as two Fermi particles with large $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values (Figs. 3 (b) and 4 (b)). In general, the threshold energy for the single photoionization ($E_{\text{single}}\left(\approx -\varepsilon(\boldsymbol{k}_{\text{HOMO}}\sigma)\right)$) and the HOMO–LUMO gaps ($\Delta E_{\text{HOMO–LUMO}}$) are closely related to the superconducting critical temperatures (T_{C}s), as shown in Fig. 1 (b). This means that not the $V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$ values of –37.137, –38.004, and –38.570 eV but the $\Delta E_{\text{HOMO–LUMO}}$ values of 9.22, 7.97, and 6.93 eV are closely related to the supercurrent critical temperatures (T_{C}) in the neutral **6an**, **10ac**, and **14ac**, respectively, as

suggested in our previous researches [1–8,11–14]. The E_{single} values are destruction energies of the spin singlet state of a Cooper pair, as listed in Table 2, as discussed in detail later.

3.3 Double-Photoionization Processes

Let us next consider the double-photoionization processes. At $E_{\text{double}} < E_{\text{photon}} < E_{\text{Cooper pair}}$, the single photoionization discussed in the previous section can be observed (Figs. 3 (b) and 4 (c)). On the other hand, due to electron correlation, the emission of two electrons by a single photon, called double-photoionization, is also possible (Figs. 3 (c) and 4 (c)). When a photon of sufficient energy is absorbed by an electron, the electron can leave the molecule, resulting in single ionization (Figs. 3 (b) and 4 (c)), or it can move along the molecule where it has a chance to hit another electron and can cause double ionization (Figs. 3 (c) and 4 (c)). These two electrons are not equivalent, and thus the E_{double} value can be defined as follows,

$$\begin{aligned} E_{\text{double}} &= -\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right) \\ &= -V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right) \\ &\quad - V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right) \\ &\approx -2\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma\right) \\ &= -2V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma\right) - 2V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma\right), \end{aligned} \quad (5)$$

where the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ value denotes the total Coulomb energy for two electrons occupying the HOMO originating from all nuclei and electrons, and the $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ value denotes the total kinetic energy for two electrons occupying the HOMO. A recent double-photoionization experiment on polyacenes [15] found that the ratio of doubly to singly charged ions increases with an increase in the molecular size from **6an** to **14ac**. This can be understood as follows. The $-\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ value decreases with an increase in the molecular size from **6an** to **14ac**. Furthermore, the dications become more significantly unstable with respect to the monocations with a decrease in molecular size from **14ac** to **6an**. This is the reason why the ratio of doubly to singly charged ions increases with an increase in the molecular size from **6an** to **14ac**.

The E_{double} values for **6an**, **10ac**, and **14ac** were reported to be 24.927, 21.391, and 20.072 eV, respectively [15]. The E_{double} values somewhat similar to the $-\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values are not so large. This can be understood as follows. Two electrons concerning the double photoionization are not equivalent (Fig. 3 (c)). Therefore, we must consider the $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values as well as the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values. The $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values are estimated to be –74.274, –76.008, and –77.140 eV, and the $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values are estimated to be 60.870, 64.434, and 66.690 eV in **6an**, **10ac**, and **14ac**, respectively. That is, both the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ and $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values are very large, but opposite in sign, each other, as shown in Fig. 2. Therefore, the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ and $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values are compensated by each other, and thus the E_{double} values somewhat similar to the $-\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values do not become very large. This is the reason why the E_{double} values are not so large. In the double- and single-photoionization, the two electrons are not equivalent, and thus the spin singlet states are destroyed. Therefore, the E_{double} as well as the E_{single} values are related to the destruction of the spin singlet state of a Cooper pair, as listed in Table 2.

3.4 Cooper Pairs Photoemission Processes

At $E_{\text{Cooper pair}} < E_{\text{photon}}$, both the single- and double-photoemission discussed in the previous section can be observed. On the other hand, there is also a possibility that the direct destruction of a Cooper pair, formed by strong attractive Coulomb interactions between two electrons with opposite momentum and spins occupying the HOMO via positively charged nuclei in **6an**, **10ac**, and **14ac**, can be observed. Two electrons forming a Cooper pair are equivalent, and thus the $E_{\text{Cooper pair}}$ value can be defined as follows,

$$\begin{aligned} & E_{\text{Cooper pair}} \\ & = -V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right) \\ & - V_{\text{kin,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right) \\ & = -V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right) \\ & >> E_{\text{double}} \approx -\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma'\right), \end{aligned} \quad (6)$$

where the $V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ value denotes the total average Coulomb energy for a Cooper pair occupying the HOMO originating from all nuclei and electrons, and the $V_{\text{kin,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ value denotes the total kinetic energy for a Cooper pair occupying the HOMO. The $E_{\text{Cooper pair}}$ values were observed to be

Table 2. The physical meanings of the E_{single}, E_{double}, ΔE_{gap}, T_c, and $E_{\text{Cooper pair}}$ values.

destruction energy (observable particle) (energy)	E_{single} (micro) (one fermion) (≈ 5~10 eV)	E_{single} (macro) (one fermion) (≈ 10^{-1}~10^{-2} eV)
our theory	destruction energy of the spin singlet state stabilized by energy gap as a consequence of quantization of orbitals	destruction energy of the spin singlet state stabilized by energy gap as a consequence of electron–phonon interactions
BCS theory	cannot be explained	destruction energy of the spin singlet state and attractive interactions between two electrons, formed by electron–phonon interactions

E_{double} (micro) (two fermions) (≈ 10~15 eV)	E_{double} (macro) (two fermions) (≈ 10^{-1}~10^{-2} eV)	ΔE_{gap} (micro) (two fermions) (≈ 5~10 eV)
destruction energy of the spin singlet state stabilized by energy gap as a consequence of quantization of orbitals	destruction energy of the spin singlet state stabilized by energy gap as a consequence of electron–phonon interactions	destruction energy of the spin singlet state stabilized by energy gap as a consequence of quantization of orbitals
cannot be explained	destruction energy of the spin singlet state and attractive interactions between two electrons, formed by electron–phonon interactions	cannot be explained

ΔE_{gap} (macro) (many fermions) (≈ 10^{-1}~10^{-2} eV)	T_c (micro) (two fermions) (≈ 5~10 eV)	T_c (macro) (many fermions) (≈ 10^{-1}~10^{-2} eV)
destruction energy of the spin singlet state formed by energy gap as a consequence of electron–phonon interactions	destruction energy of the spin singlet state stabilized by energy gap as a consequence of quantization of orbitals	destruction energy of the spin singlet state stabilized by energy gap as a consequence of electron–phonon interactions
destruction energy of the energy gap and attractive interactions between two electrons, formed by electron–phonon interactions	cannot be explained	destruction energy of the energy gap and attractive interactions between two electrons formed by electron–phonon interactions

$E_{\text{Cooper pair}}$ (one boson) (≈ 70~80 eV)
destruction energy of attractive Coulomb interactions between two electrons
cannot be explained

51.213, 51.867, and 54.358 eV, and the $E_{\text{Cooper pair, peak}}$ values were observed to be about 70~80 eV in **6an**, **10ac**, and **14ac**, respectively [16]. On the other hand, the $-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ values for **6an**, **10ac**, and **14ac** are estimated to be 74.274, 76.008, and 77.140 eV, respectively. That is, the observed $E_{\text{Cooper pair, peak}}$ values are very similar to the estimated $-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ values in **6an**, **10ac**, and **14ac**, as shown in Fig. 2. Considering that two electrons with momentum $+\boldsymbol{k}_{\text{HOMO}}\uparrow$ and $-\boldsymbol{k}_{\text{HOMO}}\downarrow$ rapidly move around a molecule, clockwise

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and counter-clockwise, respectively, the $-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)(r)$ value rapidly changes as a function of the distance (r) between two electrons, as shown in Fig. 5.

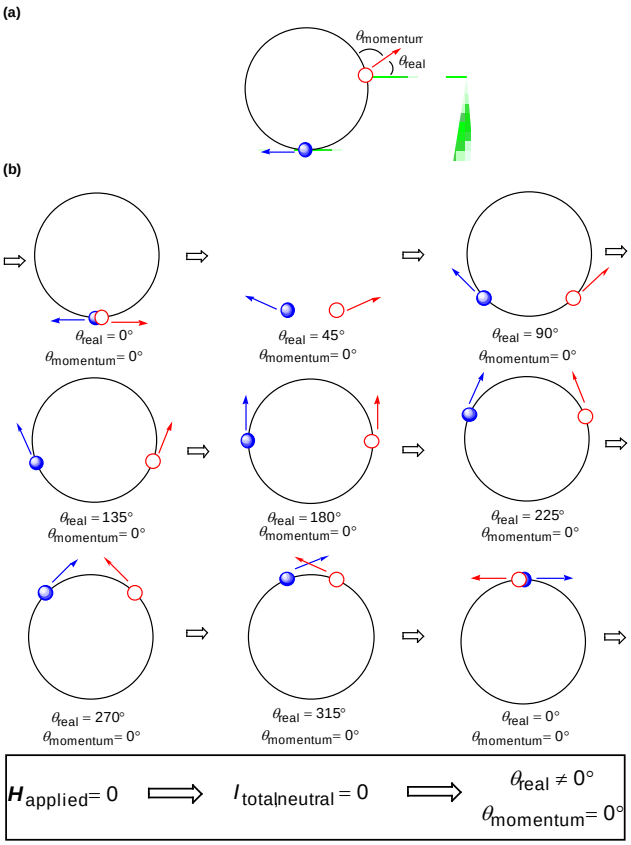

Fig. 5. (a) The definition of the angle of the movement in the second electron (opened circles) with respect to the first electron (shaded circles) in the real (θ_{real}) and momentum (θ_{momentum}) spaces. (b) Movement of two electrons occupying the HOMO in the closed-shell electronic structures in hydrocarbons. The shaded and opened circles indicate the first and second electrons moving around the molecule, clockwise and counter-clockwise, respectively.

The $-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)(r)$ value is in the range above the $E_{\text{Cooper pair}}$ values of 51.213, 51.867, and 54.358 eV, and the $-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ values of 74.274, 76.008, and 77.140 eV become similar to the $E_{\text{Cooper pair,peak}}$ values of about 70~80 eV in **6an**, **10ac**, and **14ac**, respectively, as shown in Fig. 2. That is, the observed $E_{\text{Cooper pair,peak}}$ values originate from only the $-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ values. This means that the Cooper pairs can be formed by the attractive Coulomb interactions between two electrons ($-V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$) with opposite momentum and spins occupying the same orbitals via the positive charges of nuclei, as a consequence of the Bose–Einstein condensation with zero kinetic energy, as suggested in the previous researches [1–3,11–14].

3.5 Comparison of the Cooper Pair Photoionization with the Double Photoionization

The $E_{\text{Cooper pair,peak}}$ values of about 70~80 eV are much larger than the E_{double} values of 24.927, 21.391, and 20.072 eV in **6an**, **10ac**, and **14ac**, respectively, as shown in Figs. 1 (b) and 2. This can be understood as follows. In the case of knockout mechanism, the two electrons are not equivalent, as described above, and these two electrons independently behave as two Fermi particles, and we must consider the $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values as well as the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values. Both the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values of –74.274, –76.008, and –77.140 eV and the $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values of 60.870, 64.434, and 66.690 eV in **6an**, **10ac**, and **14ac**, respectively, are very large, but opposite in sign, each other. That is, the $V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ and $V_{\text{kin}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values are compensated by each other, and thus the E_{double} values of 24.927, 21.391, and 20.072 eV somewhat similar to the $-\varepsilon\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$ values of 13.404, 11.574, and 10.450 eV in **6an**, **10ac**, and **14ac**, respectively, do not become very large. In a similar way, the $E_{\text{Cooper pair,peak}}$ can be defined as a summation of the Coulomb interactions ($V_{\text{Coulomb,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$) and the kinetic energy ($V_{\text{kin,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$) of a Cooper pair. On the other hand, since there are equivalent two electrons with opposite momentum and spins (Fig. 3 (d)), the total momentum of a Cooper pair can be zero ($\boldsymbol{k}_{\text{Cooper pair}}=\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow\right)+\left(-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)=0$), and thus the $V_{\text{kin,Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow,-\boldsymbol{k}_{\text{HOMO}}\downarrow\right)$ value can be zero. That is, the kinetic energy, which generally reduces the threshold for the photoemission in the normal fermionic electrons, and is compensated by the Coulomb energy ($V_{\text{Coulomb}}\left(\boldsymbol{k}_{\text{HOMO}}\sigma,\boldsymbol{k}_{\text{HOMO}}'\sigma'\right)$), does not play a role in the decision of the threshold for the

photoemission of the bosonic Cooper pairs. The Cooper pair can be formed by the Coulomb interactions between two electrons with opposite momentum and spins occupying the same orbitals via the positive charges of the nuclei. This is the reason why the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair, peak}}$ values are much larger than the E_{double} values in **6an**, **10ac**, and **14ac**.

The E_{double} as well as the E_{single} values are related to the destruction energy of the spin singlet state of a Cooper pair, on the other hand, the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair, peak}}$ values are related to the destruction of the attractive Coulomb interactions between two electrons of a Cooper pair occupying the HOMO, as listed in Table 2. In other words, observation of the small E_{double} and E_{single} values of about 10~20 eV means observation of just two Fermi particles (not Bose particle), on the other hand, observation of large $E_{\text{Cooper pair, peak}}$ values of about 70~80 eV [16] means that the existence of a bosonic particle with zero kinetic energy (i.e., Cooper pair) can be confirmed in the microscopic sized **6an**, **10ac**, and **14ac**, as listed in Table 2, as suggested in our previous researches [1–8,11–14].

4. Direction of the Moving of the Two Electrons in the Cooper Pair in a Molecule

Let us look into the direction of the moving of two electrons in a Cooper pair in a molecule. The definition of the angle of the movement in the second electron with respect to the first electron in the real (θ_{real}) and momentum (θ_{momentum}) spaces is shown in Fig. 5 (a).

A back-to-back emission has not been observed in the real space in the previous experimental research [16]. This can be understood as follows. For example, let us consider the case of the neutral **6an**. Movement of two electrons occupying the HOMO in the closed-shell electronic structures in hydrocarbons such as the neutral **6an** is shown in Fig. 5 (b). When magnetic (or electric) field is not applied, each electron in the HOMO would rapidly and randomly go around the molecule, $+\boldsymbol{k}_{\text{HOMO}}\uparrow$, clockwise, and $-\boldsymbol{k}_{\text{HOMO}}\downarrow$, counter-clockwise, as shown in Fig. 5 (b). Since sum of all the $\boldsymbol{k}_{\text{HOMO}}$ values is equal to zero, the total intramolecular electron mobility becomes zero ($I_{\text{total,neutral}} = 0$), as expected, when no magnetic (or electric) field is applied ($\boldsymbol{H}_{\text{applied}} = 0$ or ($\boldsymbol{E}_{\text{applied}} = 0$)), as shown in Fig. 5 (b). This can be understood from the fact that we cannot generally expect the spontaneous net charge transfer to any direction without any external applied magnetic (or electric) field. Therefore, we can reasonably expect that the θ_{momentum} value always becomes 0° (a back-to-back emission in the momentum space ($\theta_{\text{momentum}} = 0°$)). In order for the spontaneous net charge transfer to any direction not to be occurred, the θ_{momentum} value should be always zero, on the other hand, the θ_{real} value does not need to be always 0°. On the contrary, the θ_{real} value can seldom become 0°. The probability of the realization of the electronic states with the θ_{real} value of 0° would be very small (nearly zero) because of strong repulsive Coulomb interactions between two electrons as a consequence of very short distance between them. That is, a back-to-back emission can be observed not in the real space ($\theta_{\text{real}} \neq 0°$) but in the momentum space ($\theta_{\text{momentum}} = 0°$).

5. Application to the Macroscopic Sized Conventional Superconductivity

Let us next look into the macroscopic sized conventional superconductivity. In our previous researches [1–8,11–14], we suggested that electron–phonon interactions ($V_{\text{e-ph}}$) play an essential role in the forming of the closed-shell electronic structures with finite valence–conduction band gaps, by which spin singlet electronic states formed by two electrons with opposite momentum and spins ($+\boldsymbol{k}_j\uparrow$ and $-\boldsymbol{k}_j\downarrow$) occupying the same orbitals become stable, and the Coulomb interactions ($E_{\text{Cooper pair}}$ $\left(\approx -V_{\text{Coulomb, Cooper pair}}\left(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow\right)\right)$) play an essential role in the attractive interactions between these two electrons. Because of the existence of the Coulomb interactions as well as the electron–phonon interactions, electron Cooper pairs can be formed in the macroscopic sized materials, and the conventional superconducting states can appear below T_{C}, according to our previous researches [1–8,11–14].

On the other hand, according to the conventional BCS theory, the attractive electron–electron interactions and the energy gaps are formed by the electron–phonon interactions at the same time. We showed in the previous studies [1–8,11–14] that in order to form the energy gaps, two electrons are not needed at the beginning stage of the electron–phonon interactions, which are needed in the conventional BCS theory. That is, we showed that [1–8,11–14] the forming of energy gaps and attractive electron–electron interactions do not necessarily have to occur at the same time. Therefore, the finite energy gaps between the occupied and unoccupied orbitals formed by any origin (for example, by quantization of the orbitals by nature, and by electron–phonon interactions) can be related to the occurrence of superconductivity. That is, both the energy gaps ($\Delta E_{\text{gap}} = \Delta E_{\text{singlet}}$) formed by quantization of the orbitals by nature in the neutral **6an**,

10ac, and **14ac**, and those formed by electron–phonon interactions in the macroscopic sized superconductivity have equivalent physical meanings, and are closely related to the superconducting transition temperatures ($T_c \propto \Delta E_{gap}$). In any case, the electron Cooper pairs and supercurrents can be destroyed when the spin singlet states, which are stabilized by the energy gap (ΔE_{gap}) between the occupied and unoccupied orbitals, or the attractive Coulomb interactions ($V_{Coulomb,Cooper\ pair}\left(+\boldsymbol{k}_j\uparrow,-\boldsymbol{k}_j\downarrow\right)$), are destroyed. Therefore, the T_C values can be defined as follows [1–8,11–14].

$$\begin{aligned} T_c &= \min\left(\Delta E_{singlet}, -V_{Coulomb,Cooper\ pair}\left(+\boldsymbol{k}_j\uparrow,-\boldsymbol{k}_j\downarrow\right)\right) \\ &= \min\left(\Delta E_{gap}, -V_{Coulomb,Cooper\ pair}\left(+\boldsymbol{k}_j\uparrow,-\boldsymbol{k}_j\downarrow\right)\right) \\ &= \Delta E_{gap} \\ &= \Delta E_{HOMO-LUMO} \text{ for the microscopic sized materials} \\ &= V_{e-ph} \text{ for the macroscopic sized materials .} \end{aligned} \quad (7)$$

We can see from Eq. (7) that attractive electron–electron interactions are easily realized, however, the forming of the stable spin singlet states originating from the closed-shell electronic states with small energy gap between the occupied and unoccupied orbitals originating from the electron–phonon interactions is difficult to be realized in the macroscopic sized materials. That is, the T_C values in superconductivity are related not to the destruction of the attractive Coulomb interactions between two electrons but to the destruction of the spin singlet states formed by the electron–phonon interactions. On the other hand, the spin singlet states originating from the closed-shell electronic states with large energy gap between the occupied and unoccupied orbitals are formed by quantization of orbitals by nature in small sized molecules such as the neutral **6an**, **10ac**, and **14ac**. This is one of the reason why the superconductivity cannot generally be formed, and even if formed, the T_C values are usually very low in the macroscopic sized materials while the nondissipative diamagnetic currents can be usually observed at room temperatures and the T_C values are very large in small sized molecules such as the neutral **6an**, **10ac**, and **14ac**. Relative relationships between the HOMO–LUMO (valence–conduction band) gaps and the temperatures decide the electronic properties in various materials; room temperatures are very high temperatures for the closed-shell electronic states with small valence–conduction band gaps in the macroscopic sized superconductors, on the other hand, room temperatures are very low temperatures for the closed-shell electronic states with large HOMO–LUMO gaps in the small sized molecules such as the neutral **6an**, **10ac**, and **14ac**.

The E_{single} and E_{double} values similar to the $\Delta E_{HOMO-LUMO}(\propto T_c)$ values are related to the energies by which the spin singlet states formed by two electrons occupying the HOMO are destroyed, as listed in Table 2. On the other hand, the $E_{Cooper\ pair}$ and $E_{Cooper\ pair,peak}$ values are closely related to the direct destruction of strong attractive Coulomb interactions between equivalent two electrons with opposite momentum and spins occupying the HOMO, as listed in Table 2. Our previous theory [1–8,11–14] can be confirmed from the fact that all these photoionizations have been able to be observed [15,16]. On the other hand, according to the conventional BCS theory, the attractive electron–electron interactions and the energy gaps are formed by the electron–phonon interactions (V_{e-ph}) at the same time. That is, only electron–phonon interactions (V_{e-ph}) play an essential role in the attractive electron–electron interactions and the forming of the energy gaps, as listed in Table 2. In the BCS theory, the Coulomb interactions are almost completely neglected ($V_{Coulomb,Cooper\ pair}\left(+\boldsymbol{k}_{HOMO}\uparrow,-\boldsymbol{k}_{HOMO}\downarrow\right)\approx 0$) because the strong electron repulsion between two electrons occupying the HOMO can be reduced by the shielding effects as a consequence of the positive charges of nuclei. That is, according to the conventional BCS theory, the experimental results of the E_{single} and E_{double} values can be observed, but those of the $E_{Cooper\ pair}$ and $E_{Cooper\ pair,peak}$ values would not be observed. Therefore, the experimental observations of the $E_{Cooper\ pair,peak}$ values of about 70~80 eV [16] cannot be explained by the conventional BCS theory, in which the Coulomb interactions are almost completely neglected, but can be explained by our theory [1–8,11–14]. According to our theory, it can be predicted that the $E_{Cooper\ pair}$ and $E_{Cooper\ pair,peak}$ values of about 40~80 eV as well as the E_{double} values of 10^{-1}~10^{-2} eV can be observed in the macroscopic sized conventional superconductivity.

6. Concluding Remarks

In this article, we try to rationalize the experimental results for the photoemission of Cooper pairs from aromatic hydrocarbons, reported by Wehlitz et al. [16], on the basis of the hypotheses that the electron Cooper pairs in the microscopic sized molecules such as **6an**, **10ac**, **14ac**, and **18ac** can be formed by the closed-shell electronic structures with large energy gaps between the occupied and unoccupied orbitals formed by quantization

of the orbitals by nature, by which the stable spin singlet states can be formed, and large negative Coulomb interactions between two electrons with opposite momentum and spins occupying the same orbitals via the positively charged nuclei, as suggested in the previous researches [1–8,11–14].

At $E_{\text{Cooper pair}} < E_{\text{photon}}$, the direct destruction of a bosonic Cooper pair, formed by strong attractive Coulomb interactions between two electrons with opposite momentum and spins occupying the HOMO via the positively charged nuclei, as well as both the single- and double-photoemission, can be observed in **6an**, **10ac**, and **14ac**. The E_{single} and E_{double} values similar to the $\Delta E_{\text{HOMO–LUMO}}(\propto T_c)$ values are related to the energies by which the spin singlet states formed by two electrons occupying the HOMO are destroyed. On the other hand, the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair, peak}}$ values are closely related to the direct destruction of strong attractive Coulomb interactions between two electrons of a Cooper pair with opposite momentum and spins occupying the HOMO.

The $E_{\text{Cooper pair, peak}}$ values of 70~80 eV are much larger than the E_{double} values of 24.927, 21.391, and 20.072 eV in **6an**, **10ac**, and **14ac**, respectively. This can be understood as follows. In the case of knockout mechanism in the double photoionization, two electrons independently behave as two Fermi particles, and thus we must consider the $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma')$ values as well as the $V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma')$ values. The $V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma')$ and $V_{\text{kin}}(\boldsymbol{k}_{\text{HOMO}}\sigma, \boldsymbol{k}_{\text{HOMO}}'\sigma')$ values are compensated by each other, and thus the E_{double} values do not become very large in **6an**, **10ac**, and **14ac**. On the other hand, the Cooper pair can be formed by the Coulomb interactions between two electrons with opposite momentum and spins occupying the same orbitals via the positive charges of the nuclei. That is, the total momentum of a Cooper pair can be zero ($\boldsymbol{k}_{\text{Cooper pair}}(=(+\boldsymbol{k}_{\text{HOMO}}\uparrow)+(-\boldsymbol{k}_{\text{HOMO}}\downarrow))=0$), and thus the $V_{\text{kin, Cooper pair}}(+\boldsymbol{k}_{\text{HOMO}}\uparrow, -\boldsymbol{k}_{\text{HOMO}}\downarrow)$ value can be zero. That is, the kinetic energy, which generally reduces the threshold for the photoemission in the normal fermionic electrons, and is compensated by the Coulomb energy ($V_{\text{Coulomb}}(\boldsymbol{k}_{\text{HOMO}}\sigma)$), does not play a role in the decision of the threshold for the photoemission of the bosonic Cooper pairs. This is the reason why the $E_{\text{Cooper pair, peak}}$ values are much larger than the E_{double} values in **6an**, **10ac**, and **14ac**. In other words, observation of large $E_{\text{Cooper pair, peak}}$ values of about 70~80 eV means that the existence of a bosonic particle with zero kinetic energy (i.e., Cooper pair), as predicted in our previous researches [1–3,11–14], can be confirmed.

We also looked into the direction of the moving of two electrons in a Cooper pair in a molecule. In order for the spontaneous net charge transfer to any direction not to be occurred, the θ_{momentum} value should be always zero, on the other hand, the θ_{real} value does not need to be always 0°. On the contrary, the probability of the realization of the electronic states with the θ_{real} value of 0° would be very small (nearly zero) because of strong repulsive Coulomb interactions between two electrons as a consequence of very short distance between them. That is, a back-to-back emission can be observed not in the real space ($\theta_{\text{real}} \neq 0°$) but in the momentum space ($\theta_{\text{momentum}} = 0°$). This is the reason why a back-to-back emission has not been observed in the real space in the previous experimental research [16].

The E_{single} and E_{double} values similar to the $\Delta E_{\text{HOMO–LUMO}}(\propto T_c)$ values are related to the energies by which the spin singlet states formed by two electrons occupying the HOMO are destroyed. On the other hand, the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair, peak}}$ values are closely related to the direct destruction of strong attractive Coulomb interactions between two electrons with opposite momentum and spins occupying the HOMO. Our theory [1–8,11–14] can be confirmed from the fact that all these photoionizations have been able to be observed [15,16]. On the other hand, according to the conventional BCS theory, the experimental results of the E_{single} and E_{double} values can be observed, but those of the $E_{\text{Cooper pair}}$ and $E_{\text{Cooper pair, peak}}$ values would not be observed. Therefore, the experimental observations of the $E_{\text{Cooper pair, peak}}$ values of about 70~80 eV [16] cannot be explained by the conventional BCS theory, in which the Coulomb interactions are almost completely neglected, but can be explained by our theory [1–8,11–14].

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