

91 (30).

**cis-1-Ethoxycarbonyl-2-phenylcyclopropane (2bd).**

70% yield; a yellow oil; IR (neat) 1728 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.00-1.20 (m, 3H), 1.36 (ddd,  $J_{ca}=5.2$ ,  $J_{cb}=8.3$ ,  $J_{cd}=6.3$  Hz, 1H<sub>c</sub>), 1.76 (ddd,  $J_{da}=8.2$ ,  $J_{db}=8.0$ ,  $J_{dc}=6.3$  Hz, 1H<sub>d</sub>), 2.16 (ddd,  $J_{ba}=8.0$ ,  $J_{bc}=8.3$ ,  $J_{bd}=8.0$  Hz, 1H<sub>b</sub>), 2.62 (ddd,  $J_{ab}=8.0$ ,  $J_{ac}=5.2$ ,  $J_{ad}=8.2$  Hz, 1H<sub>a</sub>), 3.90-3.92 (m, 2H), 7.29-7.31 (m, 5H); MS  $m/z$  (relative intensity) 190 ( $\text{M}^+$ , 27), 145 (24), 144 (23), 135 (21), 117 (100), 91 (24).

**cis-1-n-Propoxycarbonyl-2-phenylcyclopropane (2be).**

86% yield; a yellow oil; IR (neat) 1729 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  0.78-0.83 (m, 3H), 1.30-1.33 (m, 2H), 1.37 (ddd,  $J_{ca}=8.4$ ,  $J_{cb}=8.6$ ,  $J_{cd}=6.2$  Hz, 1H<sub>c</sub>), 1.76 (ddd,  $J_{da}=8.4$ ,  $J_{db}=8.2$ ,  $J_{dc}=6.2$  Hz, 1H<sub>d</sub>), 2.16 (ddd,  $J_{ba}=8.4$ ,  $J_{bc}=8.6$ ,  $J_{bd}=8.2$  Hz, 1H<sub>b</sub>), 2.62 (ddd,  $J_{ab}=8.4$ ,  $J_{ac}=8.4$ ,  $J_{ad}=8.4$  Hz, 1H<sub>a</sub>), 3.80-3.82 (m, 2H), 7.23-7.32 (m, 5H); MS  $m/z$  (relative intensity) 204 ( $\text{M}^+$ , 3), 145 (15), 144 (12), 118 (11), 117 (100), 91 (28).

**cis-2-Phenyl-1-cyclopropanal (2bf).** 61% yield; a yellow oil; IR (neat) 1702 (C=O)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.60 (ddd,  $J_{ac}=8.4$ ,  $J_{bc}=8.4$ ,  $J_{cd}=5.7$  Hz, 1H<sub>c</sub>), 1.90 (ddd,  $J_{da}=8.4$ ,  $J_{db}=8.5$ ,  $J_{dc}=5.7$  Hz, 1H<sub>d</sub>), 2.16 (ddd,  $J_{ba}=8.4$ ,  $J_{bc}=8.4$ ,  $J_{bd}=8.5$  Hz, 1H<sub>b</sub>), 2.85 (ddd,  $J_{ab}=8.4$ ,  $J_{ac}=8.4$ ,  $J_{ad}=8.4$  Hz, 1H<sub>a</sub>), 7.24-7.39 (m, 5H), 8.69 (d,  $J=6.6$  Hz, 1H); MS  $m/z$  (relative intensity) 146 ( $\text{M}^+$ , 12), 118 (10), 117 (100), 91 (21).

**trans-2-Phenyl-1-cyclopropanecarboxylic acid.** 50% yield; a white solid; mp 87-88 °C; IR (KBr) 1682 (C=O), 3758 (OH)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR  $\delta$  1.45 (ddd,  $J_{da}=6.5$ ,  $J_{db}=8.2$ ,  $J_{dc}=4.5$  Hz, 1H<sub>d</sub>), 1.71 (ddd,  $J_{ca}=9.2$ ,  $J_{cb}=5.0$ ,  $J_{cd}=4.5$  Hz, 1H<sub>c</sub>), 1.94 (ddd,  $J_{ba}=4.0$ ,  $J_{bc}=5.0$ ,  $J_{bd}=8.2$  Hz, 1H<sub>b</sub>), 2.05 (ddd,  $J_{ab}=4.0$ ,  $J_{ac}=9.2$ ,  $J_{ad}=6.5$  Hz, 1H<sub>a</sub>), 7.12-7.16 (m, 2H, Ar), 7.24-7.36 (m, 3H); MS  $m/z$  (relative intensity) 162 ( $\text{M}^+$ , 2), 144 (9), 118 (11), 117 (100), 91 (34).

**Acknowledgment.** The present work was supported by the Organic Chemistry Research Center of the Korea Science & Engineering Foundation and by the Institute of Basic Science Research of the Ministry of Education (BSRI-95-3408).

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## Cyclic Voltammetric Study of Ferricyanide Layer Adsorbed on Gold Electrode in Sulfuric Acid Medium

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Received July 29, 1995

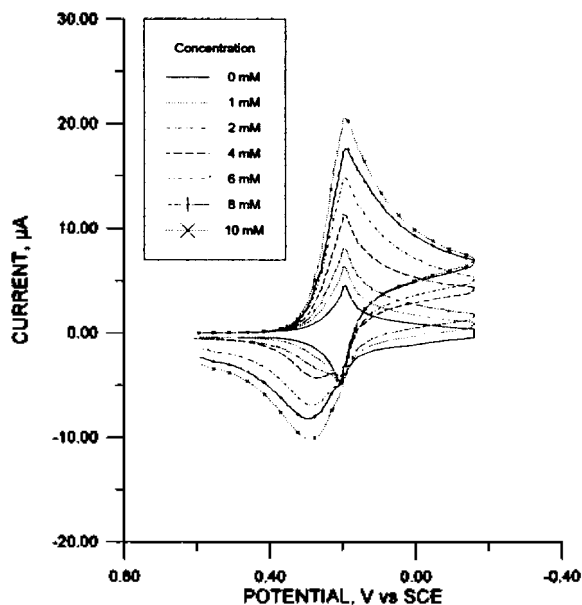
Adsorption of monolayer and subsequent formation of multilayer or thin film on the surface of various substrates in self-assembled or controlled manner have been of great concern in many fields of chemistry.<sup>1</sup> Electrochemical behaviors of adsorbed species by strong spontaneous bounding to the electrode surfaces had been studied theoretically<sup>2</sup> and experimentally.<sup>3,4</sup> Also electrochemical behaviors of thin films of mixed-valence transition metal hexacyanides on various substrates are under extensive study<sup>5,6</sup> as prospective chemically modified electrodes. In this paper, we report a cyclic voltammetric study of ferricyanide layer irreversibly adsorbed on the gold electrode surface in sulfuric acid medium, which is a well-behaving multilayer thin film formed by self-assembly methods. The proton-mediated hydrogen bonding between monolayers will be offered as the origin of binding interactions inside ferricyanide layer from our experimental results.

## Experimental section

Gold wire (diameter 1 mm and 99.99% purity from Aldrich) was sealed in a glass tube using a torr seal. Its end was polished with alumina powders (1, 0.3  $\mu$  successively) and soaked in 1:4 mixture solution of hydrogen peroxide (30%) and concentrated sulfuric acid and then rinsed thoroughly in an ultrasonic bath with distilled water. Bare gold disk electrode prepared was dipped three hours in 1 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  solution in 0.05 M sulfuric acid to attach a ferricyanide layer in self-assembled manner on its surface. Cyclic voltammetric experiments were carried out with a home-built pc-based potentiostat<sup>7</sup> adapting a conventional three electrode system. Bare gold disk electrode and ferricyanide-attached gold disk electrode prepared as above were employed as working electrodes. Saturated calomel electrode (SCE) and a platinum wire were chosen as a reference electrode and an auxiliary electrode, respectively. Chemicals were used as received without further purification.

## Results and Discussion

Cyclic voltammograms for a ferricyanide-attached gold disk electrode at different bulk concentrations of  $\text{Fe}(\text{CN})_6^{3-}$  in aqueous 1.0 M  $\text{KNO}_3$  are presented in Figure 1. Potential scan rate was fixed at 100 mV/s in the potential range of +0.6 V to -0.2 V vs. SCE. Voltammograms were obtained at 0, 1, 2, 4, 6, 8, and 10 mM of the bulk concentration of ferricyanide ion to get a concentration dependence. There are several characteristics worth to refer in the cathodic



**Figure 1.** Cyclic voltammograms for ferricyanide-attached gold disk electrode at different concentrations of  $\text{Fe}(\text{CN})_6^{3-}$  in the bulk solution. Supporting electrolyte: 1 M  $\text{KNO}_3$ . Potential scan rate: 100 mV/s. Inset: Concentrations in the bulk.

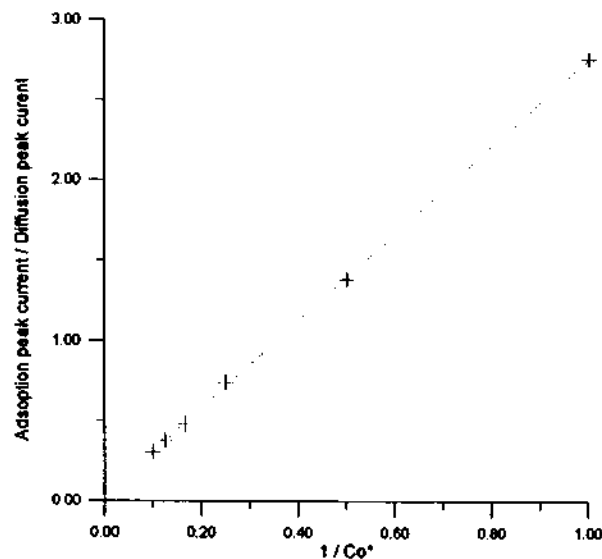
waves of Figure 1. At first, the cathodic peak current ( $i_{pc,B}$ ) due to the bulk concentration of ferricyanide is cumulated at the same potential to  $i_{pc,A}$  due to the adsorbed species on the electrode to generate the apparent cathodic peak current ( $i_{pc}$ ). The  $i_{pc,B}$  shows a linear response to the concentration of ferricyanide ion in the bulk solution. It could be specified that two processes, the electrode reaction of adsorbed species and the diffusion-controlled reaction from the bulk solution, are responsible for the electron transfer reaction at the electrode. Also one may locate that each process occurs independently under the additive way in the whole range of the cathodic wave.

If one would assume that the adsorption behavior follows the Langmuir isotherm and the electroactive adsorbates behave Nernstian in the interested potential range, the apparent peak current<sup>8,9</sup> generated from the bulk species and adsorbates could be formulated for a reversible system as following:

$$i_p = (2.69 \times 10^5) n_1^{3/2} A D_o^{1/2} v^{1/2} C_o^* + n_2^2 F^2 v A \Gamma_o^* / 4RT \quad (1)$$

where  $i_p$  is the apparent peak current (A),  $n_1$  and  $n_2$  are numbers of the electron stoichiometry involved in the diffusion-controlled electron transfer process and in the electrode reaction of the adsorbed species, respectively,  $A$  is the electrode area ( $\text{cm}^2$ ),  $D_o$  is the diffusion coefficient ( $\text{cm}^2/\text{s}$ ),  $C_o^*$  is the concentration ( $\text{mol}/\text{cm}^3$ ) of electroactive species in the bulk solution,  $v$  is the scan rate ( $\text{V}/\text{s}$ ), and  $\Gamma_o^*$  is the initial surface concentration ( $\text{mol}/\text{cm}^2$ ) adsorbed on the electrode. Other symbols in equation 1 have their conventional meanings.

From  $i_{pc}$  at 0 mM of the bulk solution (i.e., only in supporting electrolyte without adding ferricyanide ion further), the initial surface coverage of monolayer ( $\Gamma_o^*$ ) would be deter-



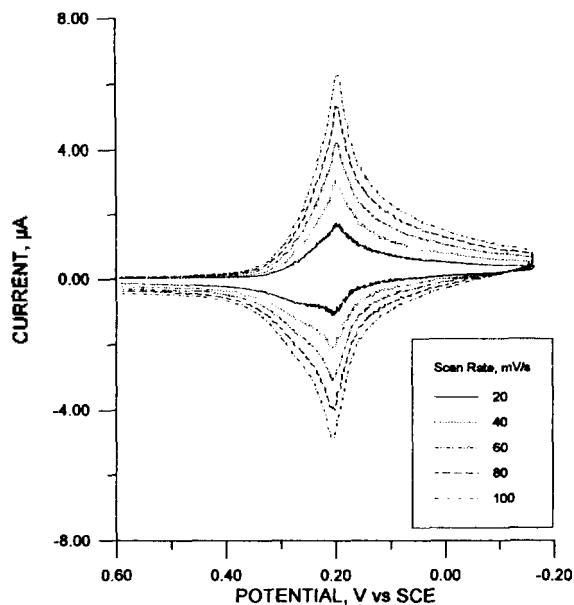
**Figure 2.** Ratio of adsorption cathodic peak current to diffusion cathodic peak current as a function of  $1/C_o^*$ .

mined as about  $6.7 \times 10^{-9} \text{ mol}/\text{cm}^2$  calculated using the second term of equation 1 where the geometric area of the electrode of  $0.785 \text{ mm}^2$  was used. Also, the area under a voltammogram curve for 0 mM of the bulk solution yields a charge of  $4.5 \text{ } \mu\text{C}$  which approximately corresponds to about  $6.6 \times 10^{-9} \text{ mol}/\text{cm}^2$  of ferricyanide adsorbed on the electrode. Either value is much larger than the monolayer coverage ( $2.6 \times 10^{-10} \text{ mol}/\text{cm}^2$ ) calculated from the cross section of ferricyanide ion (using its radius value<sup>10</sup> of about 423 pm) assuming six-coordinate two-dimensional closest packed lattice of uncharged spheres. Therefore this ferricyanide layer could be calculated to have about 25 monolayers or about 110 Å thickness if one assumes that the layer behaves like an accumulation of monolayers.

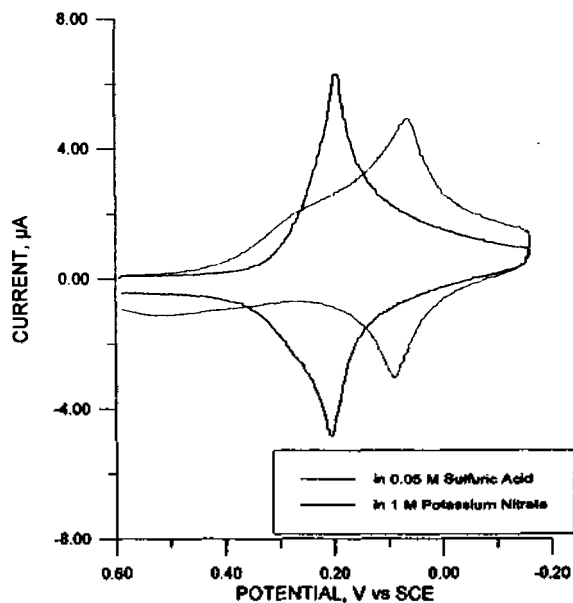
Observed ratios of  $i_{pc,A}$  to  $i_{pc,B}$  as a function of  $1/C_o^*$  present a linear dependence as presented in Figure 2. This relation was derived to get adsorption parameters due to strong adsorption of reactants on the electrode surface.<sup>2</sup>

The shape of the anodic waves, on the other hand, is quite distinct from that of the cathodic. For an increase in the bulk concentration of ferricyanide ion, the anodic peak current ( $i_{pa,B}$ ) due to diffusion from the bulk has increased in proportion. The anodic peak potential ( $E_{pa,B}$ ) due to diffusion is separated about +81 mV from  $E_{pa,A}$  of the peaks due to adsorption. While  $i_{pa,A}$  due to adsorption is supposed to remain constant, the  $i_{pa,B}$  due to diffusion is expected to increase to the bulk concentration.

The shift of the formal reduction potentials ( $E^{\circ}$ ) should be noticed. The  $E^{\circ}$  of 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 1.0 M  $\text{KNO}_3$  using bare gold disk electrode was +0.228 V vs. SCE. On close looking at the cathodic waves in Figure 1, one can find that the cathodic peak potential ( $E_{pc,A}$ ) due to adsorption is not far from and very close to the cathodic peak potential ( $E_{pc,B}$ ) due to diffusion. The  $E^{\circ}$  of the adsorption wave and of the diffusion wave in Figure 1 are +0.201 V and +0.241 V vs. SCE, respectively. The attached layer on the electrode has about 40 mV stability higher than as compared with the bulk. This could imply that it behaves like an electrode of the



**Figure 3.** Cyclic voltammograms of 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  for ferricyanide-attached gold disk electrode at different potential scan rates. Supporting electrolyte: 1 M  $\text{KNO}_3$ . Inset: Potential scan rates.



**Figure 4.** Cyclic voltammograms of 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  for ferricyanide-attached gold disk electrode in different supporting electrolytes. Thick line: in 1 M  $\text{KNO}_3$ . Thin line: in 0.05 M  $\text{H}_2\text{SO}_4$ . Potential scan rate: 100 mV/s.

second kind, *i.e.*, the electrode modification.

Cyclic voltammograms of 1.0 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 1.0 M  $\text{KNO}_3$  at different scan rates using ferricyanide-attached gold disk electrode are shown in Figure 3. The shape of waves is quite symmetrical both about the peak potentials and about the base line considering the residual current subtraction. Also,  $E_{pc}$  are quite comparable to  $E_{pa}$  which appear slightly shifted about +5 mV to anodic. But this shift is small enough to be ignored because it may be attributed to a rate-controlled adsorption-desorption process at the electrode. For the Prussian blue films on the platinum electrode, the peak potential separation was more 20 mV even at a scan rate of 5 mV/s. As seen in Figure 3, the  $E_{pa}$  is unchanged from  $E_{pc}$  with change of scan rate 20 to 100 mV. These testify that the electrode reaction of the ferricyanide/ferrocyanide redox couple is reversible and that reduced species stay adsorbed at the surface, possibly at the same strength with reactants.

In Figure 3 as in Figure 1, the cathodic waves are additive and the anodic waves have weak shoulders due to diffusion of 1.0 mM  $\text{Fe}(\text{CN})_6^{3-}$  in the bulk solution following the anodic peak due to attached species. Because the apparent  $i_{pc}$  is a sum of electrode reactions both of diffusion-controlled and of surface-adsorbed, the magnitude of  $i_{pc}$  is larger than that of  $i_{pa,B}$  due to diffusion by an amount of  $i_{pa,A}$ .

The  $i_{pa,A}$  shows a linear proportionality to the scan rate  $v$  in the experimental range 20 to 100 mV/s as expected for the adsorbed species.<sup>2,3</sup> This leads a strongly adsorbed layer on the electrode surface. On taking a good look at Figure 3, the peak shape of voltammograms obtained are not quite the same as that of monolayers, *e.g.*, 9,10-phenanthrenequinone adsorbed on the pyrolytic graphite electrode previously reported.<sup>4</sup> Those voltammograms of monolayers were well fitted and described with a parameter of the surface activity coefficients<sup>11</sup> to the  $i$ - $E$  curve equation (the sec-

ond term of equation 1) derived from the Langmuir isotherm and the Nernst equation. This equation shows an exponential increase and decay at both sides of the peak and a smooth round shape around the peak. One can find clearly that the peak shapes at  $E_{pc}$  or  $E_{pa}$  are rather sharp not smooth. This kind of a sharp peak was observed in cyclic voltammograms of thin films of mixed-valence transition metal hexacyanides.<sup>5</sup> But both  $E_{pc}$  and  $E_{pa}$  are at the almost same position without any appreciable shift (less 5 mV) at a relatively fast scan rate.

Cyclic voltammogram of 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 0.05 M  $\text{H}_2\text{SO}_4$  using ferricyanide-attached gold disk electrode at scan rate of 100 mV/s is presented in Figure 4. To look at the dependence of voltammograms on the supporting electrolyte, the curve obtained in 1 M  $\text{KNO}_3$  is shown together. The adsorption peak, which is termed a postpeak or a postwave, is separated far to cathodic from the diffusion-controlled peak in the cathodic and as well in the anodic wave. This could pose the greater stability of ferricyanide layer in sulfuric acid medium. When the reactant species are very strongly adsorbed on the electrode surface, a postpeak<sup>2</sup> is expected to appear separated from the diffusion-controlled peak.

Cyclic voltammogram of the adsorbed species in sulfuric acid has several distinctions from that in  $\text{KNO}_3$ . At first, the difference between  $E_{pc}$  of the diffusing species, +0.414 V vs. SCE and  $E_{pa}$  of the adsorbed species, +0.070 V vs. SCE is as much as 0.344 V. Considering that  $E^v$  of 1 mM  $\text{Fe}(\text{CN})_6^{3-}$  in 0.05 M  $\text{H}_2\text{SO}_4$  using bare gold disk electrode was 0.324 V vs. SCE, it could be settled that the ferricyanide-attached gold electrode is a modified electrode. The peak current is about 40% less than that in  $\text{KNO}_3$ . Also, The peak shape is slightly less sharp and more broad compared to that in  $\text{KNO}_3$ . It could point to less mobility of ions inside the layer or close-packing in the attached layers. If one

would apply the second term of equation 1 to a postpeak current to calculate the initial surface coverage on the electrode surface, it would be determined as about  $4.1 \times 10^{-9}$  mol/cm<sup>2</sup>. It corresponds to about 16 monolayers and about 66 Å thickness as before. The fact that the peak separation is about 27 mV larger than that in KNO<sub>3</sub> means that the redox reaction of ferricyanide/ferrocyanide at the electrode in sulfuric acid medium is less electrochemically reversible and less mobile than in KNO<sub>3</sub>.

The preparation of ferricyanide layer on the gold electrode surface on the acidic medium yields a considerable thickness of multilayer which is behaving well in the electrochemical environments. This layer is even strongly molded in an acidic supporting electrolyte than in a neutral. The protons are known to bound to the nitrogen atoms of the CN groups of the ferrocyanide ion with intermolecular hydrogen bonding in the solid phase.<sup>12</sup> The origin of interactions which are responsible for adsorption or binding of ferricyanide to the gold surface in the self-assembly manner is not clearly understood yet, Brønsted interactions mediated by protons or Lewis interactions through Lewis acid site on the surface is one of the prospects.<sup>13</sup> To account for the formation of a multilayer on the surface, the interactions between monolayers should be addressed. Right now, from our experimental results we could propose a possibility of the proton-mediated hydrogen bonding between monolayers to generate a well-behaving multilayer of ferricyanides on the gold surface.

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### **Ab Initio Study of Rare Gas-Hydrogen Ionic Cluster R<sub>2</sub>H<sup>+</sup> (R=He, Ne, Ar)**

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*Received August 8, 1995*

The simple rare gas-hydrogen ionic clusters of R<sub>2</sub>H<sup>+</sup> (R = He, Ne, Ar) are interesting species in that they represent the prototype of weakly bound (De ~ 10 kcal/mole) molecular ions with the valence-active hydrogen which can serve as a medium to form more complex clusters. The formation of several rare gas-hydrogen molecular ions such as R<sub>n</sub>H<sup>+</sup> (R = He, Ne, Ar; n = 1, 2, 3, 4) in gas phase and in inert rare gas matrices can be facilitated not only by polarization forces between interacting partners but also by the special role proton can provide between essentially non-attractive rare gas atoms.<sup>1</sup> There have been many experimental and theoretical studies indicating the existence of stable rare gas-hydrogen ionic species.<sup>2-18</sup> In a collision experiment between R<sub>2</sub><sup>+</sup> and H<sub>2</sub> using flowing afterglow technique,<sup>3</sup> Adams, Bohme and Ferguson observed that either RH<sup>+</sup> or R<sub>2</sub>H<sup>+</sup> could be dominant species in rare gas-hydrogen mixture in gas phase, depending upon hydrogen gas flow rate and rare gas ions. Although there have been a number of theoretical investigations on diatomic rare gas-hydrogen ionic species, there have been a few studies on triatomic and more complex ionic species, especially for Ne and Ar species, probably due to the number of electrons involved in the calculation and, more importantly, their non-valent (non-octet) electronic structures.

The most extensive theoretical study on R<sub>2</sub>H<sup>+</sup> has been carried out by Matcha *et al.* based on *ab initio* Hartree-Fock Self-Consistent-Field (HF-SCF) calculations.<sup>12-14</sup> They calculated the equilibrium geometry and binding energy for these species as well as vibrational frequencies. They found that all species have linear symmetric equilibrium geometry (*D<sub>∞h</sub>*) and concluded that the bonding is basically due to the combination of charge induced dipole attractions resulting from the polarization of the rare gas atoms by the relatively unshielded proton charge and the repulsive exclusion forces resulting from the overlapping of the charge clouds centered on the rare gas atoms for He and Ne species. For Ar species, their results are unreliable due to the incompleteness of the basis set used in the calculation. More recently, Last and George<sup>19</sup> suggested the equilibrium geometry of Ar<sub>2</sub>H<sup>+</sup> to be slightly bent and unsymmetrical, based on semiempirical diatomics in ionic systems (DIIS) method.<sup>20,21</sup> However,