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Raman Spectra of the Adducts of Reduced Species of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ with Acetylene

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Reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ form adducts with acetylene (C_2H_2 or C_2D_2) in dry CH_3CN with liberating a terminal PhS^- ligand. The $\nu(C\equiv C)$ Raman band undergoes 45 to 70 cm^{-1} low frequency shifts upon coordination of acetylene to the clusters.

Nitrogenase (N_2ase) composed of iron and molybdenum-iron proteins involving Fe_4S_4 and molybdenum-iron-sulfur clusters, respectively, can catalyze the reductions not only of N_2 but also of a variety of small unsaturated molecules such as C_2H_2, RCN, RNC, and N_3^-.1) In the absence of any substrates, N_2ase reduces protons to evolve H_2, whose amount decreases with increasing the substrates added. In the reduction of C_2H_2 saturated in water by N_2ase, C_2H_2 consumes almost all electrons transfered from N_2ase, practically inhibiting H_2 evolution.2) Moreover, the reduction of C_2H_2 by N_2ase in D_2O affords *cis*-$C_2D_2H_2$ selectively.1) Based on such a specifically catalytic activity of N_2ase toward C_2H_2, the reduction of C_2H_2 has been utilized for evaluating the activity of N_2ase. On the other hand, the reduced cluster $[Fe_4S_4(SPh)_4]^{3-}$ can reduce C_2H_2 in the presence of CH_3COOD to afford *cis*-$C_2D_2H_2$.3) In addition, not only $[Fe_4S_4(SPh)_4]^{2-}$ but also $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ reduce C_2H_2 to afford C_2H_4 catalytically in MeOH/THF (1:1 v/v) under controlled potential electrolysis conditions, where H_2 evolution practically stopped in the C_2H_2-saturated solution; the reduction has been suggested to proceed via the 1:1 adduct of $[Fe_4S_4(SPh)_4]^{3-}$ with C_2H_2, based on the kinetic study.4) It may, therefore, be essential to elucidate the interaction of acetylene with Fe-S and Mo-Fe-S clusters in connection with the mechanism of the reduction of C_2H_2 by N_2ase. This letter reports the Raman and electronic spectral evidence for the adduct formation of C_2H_2 and C_2D_2 with the reduced species of $[Fe_4S_4(SPh)_4]^{2-}$ 5) and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$.6)

The Raman spectra of the oxidized and electrochemically reduced species of

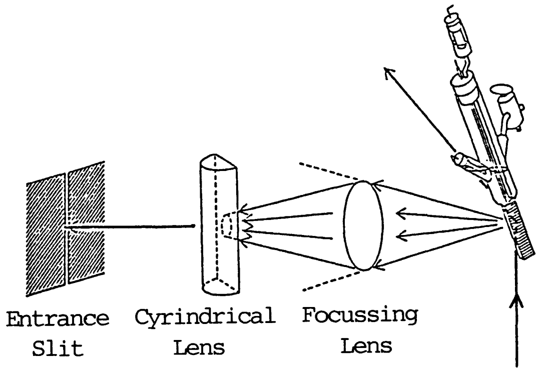

Fig. 1. Arrangement of an electrolysis cell in the Raman spectrometer.

the clusters were measured with a JASCO R-500 spectrometer equipped with a cylindrical lens and a focussing lens in order to collect a scattered light effectively, by using a thin layer electrode cell (cell length 0.5 mm)[7] with a Pt disk electrode, as shown in Fig. 1. Electronic spectra of both clusters show a strong absorption band around 450 nm due to the CT transition from thiolate sulfur to iron. Thus, the resonance Raman spectra of iron-sulfur proteins and synthetic iron-sulfur clusters have been obtained by irradiation of a 457.9 and 488.0 Ar^+ laser beam.[8] However, the reduced species of the present clusters prepared by the controlled potential electrolysis of *n*-Bu_4N salts of $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ at -1.10 V *vs*. SCE in C_2H_2-saturated CH_3CN have been unstable to those laser beams; prolonged irradiation of a 488.0 nm laser beam with more than 8 mW power to the clusters resulted in the formation of a black deposit on the working electrode. The Raman spectra were, therefore, obtained by irradiation of a 514.5 nm laser beam with less than 20 mW power[9] to the Pt working electrode in the thin layer electrode cell.

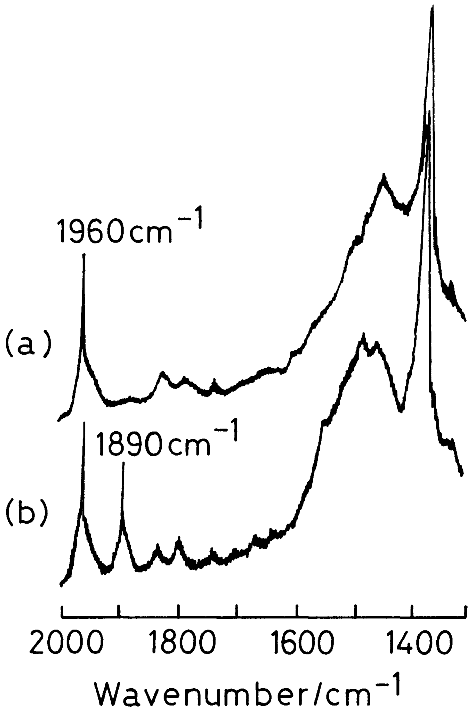

Fig. 2. Raman spectra of C_2H_2-saturated CH_3CN solutions containing $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$ (1.0 x 10^{-3} mol dm^{-3}) before (a) and after (b) the electrolysis at -1.10 V *vs*. SCE.

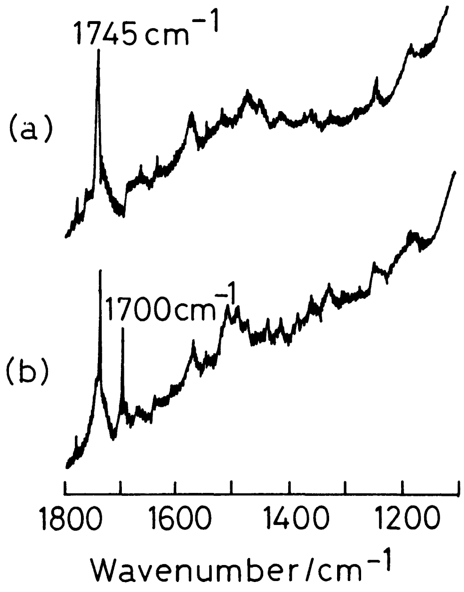

Fig. 3. Raman spectra of C_2D_2-saturated CD_3CN solutions containing $(n\text{-}Bu_4N)_2[Fe_4S_4(SPh)_4]$ (1.0 x 10^{-3} mol dm^{-3} before (a) and after (b) the electrolysis at -1.10 V *vs*. SCE.

A C_2H_2-saturated CH_3CN[10)] solution of $[Fe_4S_4(SPh)_4]^{2-}$ exhibits a ν(C≡C) Raman band at 1960 cm^{-1} together with strong bands at 1450 and 1375 cm^{-1} due to the solvent molecule (Fig. 2a). The controlled potential electrolysis of the solution at -1.10 V *vs*. SCE[11)] results in the appearance of an additional band at 1890 cm^{-1} (Fig.2b), which disappeared upon reoxidation of the resulting solution by the electrolysis at -0.65 V *vs*. SCE, while the remaining bands were unchanged. Similarly, a C_2D_2-saturated CD_3CN solution of $[Fe_4S_4(SPh)_4]^{3-}$ prepared under the same electrolysis conditions display a new band at 1700 cm^{-1} together with the free ν(C≡C) band at 1745 cm^{-1} (Fig. 3), and the former completely disappeared upon reoxidation of the solution at -0.60 V *vs*. SCE. These results suggest that C_2H_2 and C_2D_2 are coordinated with the reduced species $[Fe_4S_4(SPh)_4]^{3-}$ in solution, while they do not with the oxidized species $[Fe_4S_4(SPh)_4]^{2-}$. Analogously, the controlled potential electrolyses of $(Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ in C_2H_2-saturated and C_2D_2-saturated CD_3CN solutions at -1.10 V *vs*. SCE[12)] display ν(C≡C) bands of coordinated acetylene at 1900 and 1695 cm^{-1}, respectively, (Fig. 4a and 4b), which disappeared upon reoxidation of these solutions at -0.60 V *vs*. SCE.

The adduct formation between the reduced species of the present clusters and acetylene is consistent with the electronic absorption spectra of the reduced species $[Fe_4S_4(SPh)_4]^{3-}$ in C_2H_2-saturated CH_3CN, which shows an absorption band centered at 306 nm assignable to the PhS^- anion[13)] (a dotted broken line in Fig. 5), whereas no band at 306 nm appears in the spectrum either of the reduced species in C_2H_2-free CH_3CN (a broken line in Fig. 5) or of the oxidized species $[Fe_4S_4(SPh)_4]^{2-}$ in C_2H_2-

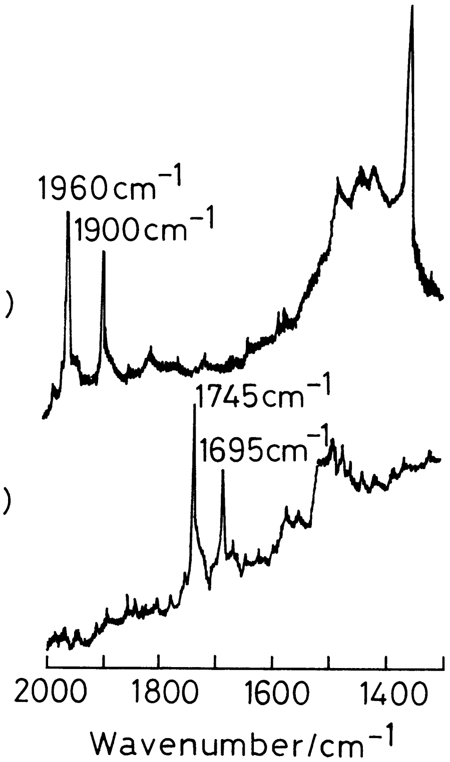

Fig. 4. Raman spectra of C_2H_2-saturated CH_3CN (a) and C_2D_2-saturated CD_3CN (b) solutions containing $(n\text{-}Bu_4N)_3[Mo_2Fe_6S_8(SPh)_9]$ (1.0 x 10^{-3} mol dm^{-3}) after the electrolysis at -1.10 V *vs*. SCE.

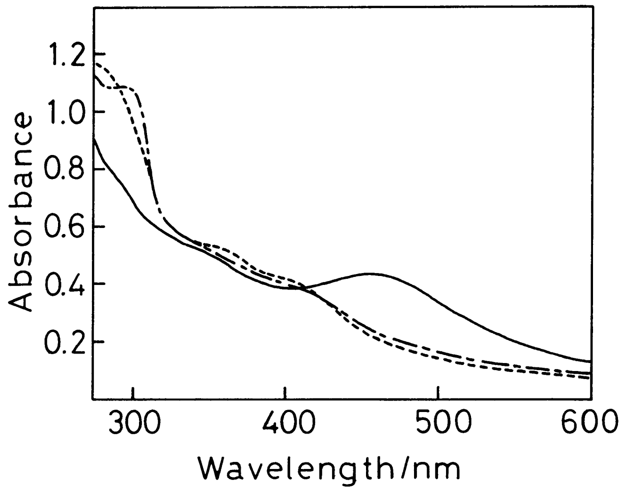

Fig. 5. Electronic absorption spectra of $[Fe_4S_4(SPh)_4]^{2-}$ in C_2H_2-free and -saturated CH_3CN (——), $[Fe_4S_4(SPh)_4]^{3-}$ in C_2H_2-free CH_3CN (----), and in C_2H_2-saturated CH_3CN (—-—); the concentration of the cluster 5.0 x 10^{-4} mol dm^{-3}.

free and C_2H_2-saturated CH_3CN (a solid line in Fig. 5). In addition the reoxidation of $[Fe_4S_4(SPh)_4]^{3-}$ in C_2H_2-saturated CH_3CN at -0.60 V *vs.* SCE for 1 h almost recovered the spectrum of $[Fe_4S_4(SPh)_4]^{2-}$ (a solid line in Fig. 5).14) Similarly, the electrolysis of $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ at -1.10 V *vs.* SCE in C_2H_2-saturated CH_3CN exhibits the 306 nm band, which disappeared upon reoxidation of the solution at -0.60 V *vs.* SCE.

Thus, both $[Fe_4S_4(SPh)_4]^{2-}$ and $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ are coordinated with acetylene upon electrochemical reduction to the 3- and 4- states, respectively, with liberating a terminal PhS^- ligand. Such a ligand substitution has been reported for the reaction of $[Mo_2Fe_6S_8(SPh)_9]^{4-}$ with CH_3N_3, in which CH_3N_3 coordinates to iron with liberating a terminal PhS^- ligand to form the 1:1 adduct.15) It should be mentioned that upon coordination of C_2H_2 and C_2D_2 to the present clusters, the $\nu(C{\equiv}C)$ band undergoes only 45 to 75 cm^{-1} low frequency shifts, which are much smaller than those upon coodination of 1,2-disubstituted acetylenes to the mononuclear metal complexes; 130 - 200 cm^{-1},15) suggesting weak interactions of C_2H_2 and C_2D_2 with the present clusters.

References

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9) The present clusters decomposed upon irradiation of 514.5 nm with more than 25 mW beam power.
10) CH_3CN and CD_3CN distilled three times over CaH_2 under dry N_2 were saturated with C_2H_2 and C_2D_2, respectively (1.58×10^{-1} mol dm^{-3}).
11) The $[Fe_4S_4(SPh)_4]^{2-/3-}$ redox potential is -1.04 V *vs.* SCE.
12) $[Mo_2Fe_6S_8(SPh)_9]^{3-}$ underdoes two successive redox reactions of the 3-/4- and 4-/5- couples at -1.02 and -1.23 V *vs.* SCE, respectively.
13) The absorptivity at 306 nm (ε_M= 19800 mol^{-1} dm^3 cm^{-1}) indicated that 0.25 mole of PhS^- per one mole of $[Fe_4S_4(SPh)_4]^{2-}$ is dissociated.
14) The intensity at λ_{max} (448 nm) of $[Fe_4S_4(SPh)_4]^{2-}$ is recovered by 98%.
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