Protection, Size Factors, and Reaction Dynamics of Colloidal Redox Catalysts Mediating Light Induced Hydrogen Evolution from Water

John Kiwi and Michael Grätzel*

Contribution from the Institut de Chimie Physique, Ecole Polytechnique Fédérale, Lausanne, Switzerland.

Received May 29, 1979

Abstract: Dimethyl viologen (MV^{2+}) is photoreduced to the cation radical in an aqueous solution containing $Ru(bpy)_3{}^{2+}$ as a sensitizer and EDTA as an electron donor. The efficiency of colloidal platinum to mediate hydrogen generation from water via $2MV^+ + 2H_2O \rightarrow H_2 + 2OH^- + 2MV^{2+}$ is influenced by both the nature of the protective colloid and particle size. A centrifuged, poly(vinyl alcohol) stabilized catalyst having a particle radius of 110 Å showed exceptionally high activity in promoting the above-mentioned reaction. With such a preparation, for the first time, a direct observation was made of the kinetics of MV^+ interaction with the Pt particles. The reoxidation of MV^+, according to eq 1, occurs in only 15 μs at 10^{-3} M Pt and leads to stoichiometric formation of H_2. The quantum yield of H_2 formation in such a system was determined as 0.13 ± 10%.

Introduction

It has been ascertained presently through a number of studies that certain noble metal dispersions are suited to mediate light induced hydrogen[1] and oxygen evolution[2] from water. The eventual use of these redox catalysts in solar energy conversion systems still warrants detailed investigations leading to a better understanding of their action and an improvement of their efficiency.

In the present work, an aqueous system is employed[1c,d] in which under visible light illumination methyl viologen (MV^{2+}) is irreversibly reduced to the radical MV^+. The process of interest is the subsequent reduction of water by MV^+

$$2MV^+ + 2H_2O \xrightarrow{Pt} 2MV^{2+} + H_2 + 2OH^- \qquad (1)$$

which is mediated by Pt particles of colloidal dimension. It will be shown that both the particle size as well as the nature of the protective colloid employed affect the rate of hydrogen evolution. For the first time, observations will be reported illustrating directly the dynamics of intervention of the Pt particles in the redox events.

Experimental Section

The following procedure was applied in the preparation of colloidal Pt-poly(vinyl alcohol) solutions (Pt-PVA): 20 mL of poly(vinyl alcohol), mol wt 60 000, 2% solution, was added to 50 mg of H_2PtCl_6. This solution was neutralized with NaOH to pH 8.0 and heated to 100 °C for half an hour, and water was added to a total volume of 40 mL. Hydrogen gas was then passed through the solution until it became dark grey-brown indicating that Pt deposition has taken place. This reduction probably involves the species[3] $Na_2PtCl_3(OH)_3$. The pH after reduction becomes slightly acidic.

It has been recognized since 1954 that the catalysts obtained from supernatant fractions of centrifuged metal-PVA catalysts are by far the most active per milligram of metal.[4] Centrifuged samples of Pt-PVA-60 000 catalyst have been prepared under different time and spinning conditions as shown in Table I. The supernatant was found to contain lighter particles, while the heavier particles are found in the deposit. About 20% of the initial Pt is in the supernatant when centrifugation takes place at 20 000 rpm (50000*g*) and the rest is in the residue.

Pt-poly(acrylic acid) hydrazide was prepared as previously described,[5] keeping the molar ratio of protective agent and Pt as reported in this paper for gold acrylate solutions. Pt-PVA-pyrrolidone has been also prepared following the same reference. The Pt/polymer ratio corresponded to the value where the protective action of the polymer was reported to be optimal. Similarly in the cases where the preparation of the Pt catalyst was adapted from other metals (Ag or Au), the same optimal ratio in moles of metal per moles of protective colloid was employed.

Pt-cetyltrimethylammonium chloride (CTAC) was prepared by adding 84 mg of CTAC (Eastman) to a 100-mg $PtCl_4$ solution (30 mL) at pH 8. The reduction of Pt is carried out by H_2 until a dark grey color appears. A clear solution is obtained after 1-h centrifugation at 20 000 rpm. We report here for the first time that a surfactant acts as protective agent for metal platinum in photolytic reactions.

Hydrazine sulfate has been reported to be highly effective in producing finely subdivided Ag by reduction.[6] This principle has been used here to reduce H_2PtCl_6 to Pt and the metal obtained this way has subsequently been used in catalysis. The Pt-phosphorus, Pt-TiO_2, and Pt-citric acid catalyst has been prepared by the procedures indicated for gold[7] and adapted here to Pt. Gelatine (Fluka 180 Bloom) derived from the natural protein collagen broken into about 30 amino acids has been used at 0.1% concentration as a protective agent.[8]

Correlation function measurements to determine the size of the particles were carried out by low angle light scattering on a Chromatix KMX-6 instrument (Chromatix, 560 Oakmead Parkway, Sunnyvale, Calif. 94086), equipped with a 64-channel digital correlator. Diffusion measurements were carried out in homodyne experiments, and the particle size was derived from the correlation times by means of the Stokes-Einstein relation.

Steady-state irradiations were carried out with 20-mL solutions using an Osram XBO 450-W lamp in conjunction with a light filter ≤400 nm (Schott GmbH). A 15-cm water cell absorbed the infrared light. A ferrioxalate chemical dosimeter[9] was employed to measure the photon flux. Hydrogen was analyzed by means of a Gow-Mac thermal conductivity detector with a limit of 0.1 μmol. The column used at 35 °C was a Carbosieve 5A. In the case of the more active catalysts, direct volumetric measurement of the evolved hydrogen was possible.

Laser photolysis experiments were performed with a J.K. frequency doubled neodymium laser. The Q-switched pulse had a duration of 20 ns (HWHH). The details and detection method have been reported previously.[1c]

Results and Discussion

(i) Nature of the Protective Colloid. The aqueous solutions employed in the experiments contained $Ru(bpy)_3{}^{2+}$ as a sensitizer, MV^{2+} as an electron acceptor and EDTA as an electron donor. The details of the redox processes leading to MV^{2+} reduction have been reported earlier.[1c,d] In the presence of colloidal platinum, MV^+ is reconverted into MV^{2+} under simultaneous evolution of hydrogen from water. In Figure 1 are reported hydrogen evolution rates obtained from Pt dispersions that were prepared in the presence of a variety of protective colloids. The irradiated solutions had a volume of 25 mL and contained 1 mg of Pt. We did not attempt to optimize experimental parameters such as sample size, illumination conditions, and solution concentrations, etc. to obtain a maximum H_2 yield, our interest being centered on the relative efficiency of the different catalyst preparations. As for the MV^{2+} concen-

0002-7863/79/1501-7214$01.00/0

Table I

sample	concn, mg of Pt/25 mL of soln	diffusion, 10^{-7} cm^2/s	R_H, Å	centrifugation time, h	centrifugation, rpm
Pt-PVA-60 000	3.5^a	2.05	110	10	20 000
Pt-PVA-60 000	3.5^a	0.73	320	8	13 000
Pt-PVA-60 000	3.5^a	0.67	360	2	13 000
Pt-PVA-60 000	3.5	0.45	530	0	
PVA-60 000	0	2.10	105	0	

[a] After centrifugation.

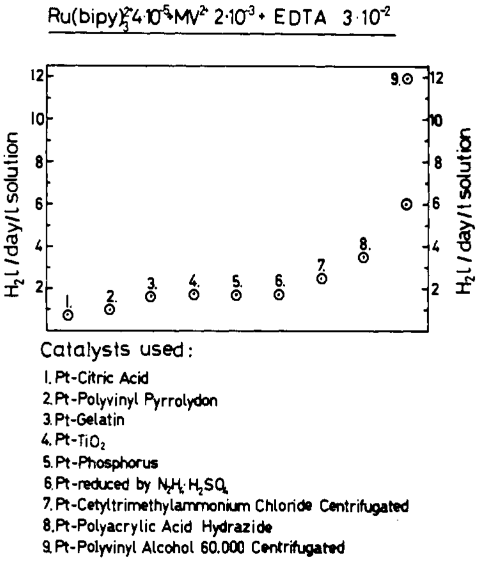


Figure 1. Evolution of H_2 of a solution of 4×10^{-5} M Ru(bpy)$_3{}^{2+}$, 2×10^{-3} M MV^{+2}, 3×10^{-2} M EDTA at pH 5, irradiation with light, $\lambda > 400$ nm, in the presence of various catalysts as indicated. For preparation of catalyst 9, the higher point contains 3.5 times the amount of Pt as the lower point.

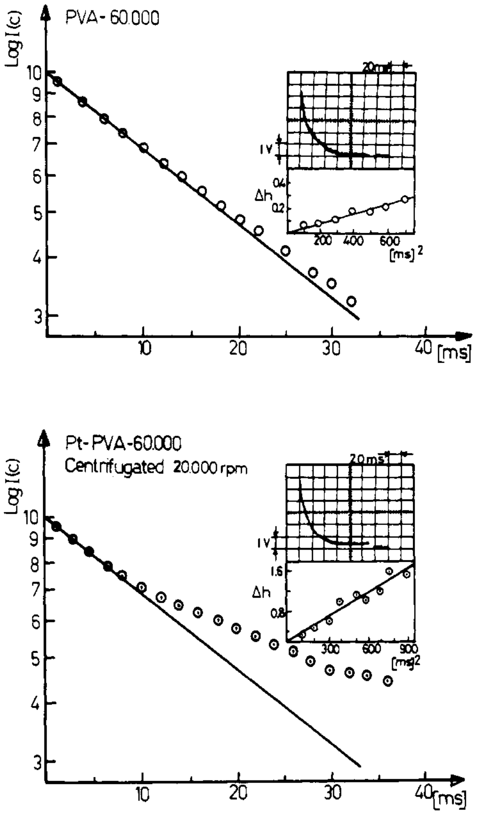


Figure 2. Autocorrelation function for poly(vinyl alcohol) polymer and Pt-PVA-60 000 at $\theta = 4.5°$. Sample time 2 ms; data acquisition time 10 min; concentration in PVA 3.3×10^{-4} M. In the ordinate, 1 V is equivalent to 0.2×10^{20} counts full scale in both inserts. Abscissa: time scale in milliseconds.

tration, 2×10^{-3} M represents an optimum value. At lower concentrations the electron transfer quenching is not efficient enough to compete with nonreactive deactivation of excited Ru(bpy)$_3{}^{2+}$. A too high MV^{2+} content ($>3 \times 10^{-3}$ M), on the other hand, has an adverse effect on the H_2 evolution rate since the thermodynamics of reaction 1 become unfavorable and possibly due to absorption of MV^{2+} on Pt. From catalyst one to eight one notices a gradual increase in activity. With nine, exceptionally high evolution rates are obtained. This catalyst was prepared by centrifuging a conventional Pt/PVA colloid for 8 h at 20 000 rpm. Through this procedure one removes heavier particles; in the transparent supernatant, solution remains about 20% of the initial amount of Pt in very finely dispersed form. From these results one infers that apart from the nature of the protective colloid it is the size of the Pt aggregates that is crucial for the catalytic activity. This effect will now be examined in more detail.

(ii) Size Factors. Figure 2 shows correlation functions obtained from aqueous solutions containing the protective colloid PVA alone and in the presence of Pt. For the former solution, the linearity of the semilog plot is relatively good; the slope of the straight line gives a hydrodynamic radius R_H = 105 Å. This result demonstrates the applicability of the quasielastic light scattering technique to determine the particle size in PVA solutions. In a monodisperse system a simple exponential would have been obtained. The good semilogarithmic fit noted in the upper part of Figure 2 shows that the PVA aggregates have a relatively narrow size distribution. A quantitative assessment of the width of the distribution can be made from the behavior of the autocorrelation function at longer times. In this domain the experimental points deviate from linearity. The insert shows that the deviation $\Delta h = \Delta \log I$ increases proportionally to t^2. The polynomial fit to the time dependency of the correlation function yields[10]

$$\Delta h = K^4 D^2 v t^2 \tag{2}$$

where K is the modulus for the scattering vector (K = 1.039 $\times 10^{-4}$ cm^{-1}), D is the diffusion coefficient of the particle and v is the polydispersity index. For the latter parameter, one obtains $v = 0.14$ indicating a relatively narrow size distribution of the PVA. A similar analysis for the centrifuged Pt colloid gives R_H = 110 Å and $v = 0.66$. This indicates that the Pt particle size is small compared with that of the polymer forming the protective envelope. However, the polydispersity of the Pt/PVA particles is significantly greater than that of PVA alone.

By varying time and speed of centrifugation, Pt/PVA colloids with different particle size were prepared. The experimental parameters are listed in Table I. In order to compare the efficiency of these preparations, the same Pt concentration in solution had to be achieved. The losses incurred by centrif-

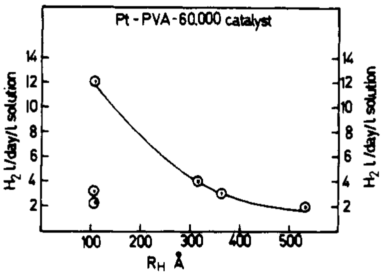


Figure 3. Correlation for the observed yields for H_2 in the system 4×10^{-5} M $Ru(bpy)_3{}^{2+}$, 10^{-3} M MV^{2+}, 3×10^{-2} M EDTA at pH 5 and the radius of the catalysts employed. Catalysts were prepared as stated in Table I. The lower points at 110 Å contain 0.2 mg of Pt and 0.3 mg of Pt per 25 mL of solution, respectively.

ugation were accounted for by increasing the amount of starting material. The concentration of catalyst was determined from weighing the residue after washing with ether and drying and also from measuring the Pt content of the solution directly via atomic absorption spectroscopy. The particle size has a decisive influence on the activity of the catalyst. This is illustrated in Figure 3 where the relationship is given between the radius of the Pt/PVA aggregates and their activity in producing H_2 under irradiation of the solutions.

It is seen that a decrease of the radius from 500 to 100 Å leads to a drastic augmentation of the hydrogen evolution rate which is as high as 12 L day^{-1} L^{-1} solution for the smallest particle size. In fact, in the last case, the bubbling of hydrogen gas occurring under illumination of the solution is readily seen. Figure 3 also shows that the yield of H_2 obtained with the most active catalyst is a function of the Pt concentration. For example, if 0.8 mg of Pt/100 mL of solution is used, the yield is five to six times smaller than with 12 mg/100 mL.

The size effects observed may be explained by the fact that the Pt particles intervene as microelectrodes in the hydrogen evolution reaction (eq 1).[11] Electron transfer from MV^+ to the Pt particles tunes these microelectrodes cathodically until H_2 formation can take place. A smaller electrode size is advantageous both from the viewpoint of mass transport of the electroactive species as well as surface area per gram of catalyst employed. It is interesting to note that, under our experimental condition, the speed of electron turnover in the MV^+/MV^{2+} relay—and not the photon flux or the kinetics of MV^{2+} photoreduction—is rate determining in the hydrogen generation process. Evidently, from these results, it is desirable to develop catalysts with a minimum particle size and narrow size distribution. Work in this direction using new types of polymers as protective agents is in progress.

(iii) Direct Observation of the MV^+ Reoxidation by Colloidal Pt. A further advantage of the centrifuged Pt/PVA is that the solutions remain completely transparent even at high catalyst concentration. This allows one to study directly the dynamics of the reaction of MV^+ with Pt particles by employing a laser photolysis technique. The upper part of Figure 4 shows oscilloscope traces illustrating the temporal behavior of the characteristic MV^+ absorbance at 602 nm in the absence and presence of catalyst. The upward deflection of the signal after the laser pulse is due to the formation of MV^+ via the photo redox process.[1c,d]

$$^*Ru(bpy)_2{}^{2+} + MV^{2+} \rightarrow Ru(bpy)_2{}^{3+} + MV^+ \quad (3)$$

where $^*Ru(bpy)_3{}^{2+}$ stands for the charge transfer excited state of the ruthenium complex. $Ru(bpy)_3{}^{3+}$ is reconverted to the 2+ oxidation state by EDTA (HY^{3-}):

$$HY^{3-} + Ru(bpy)_3{}^{3+} \rightarrow Ru(bpy)_3{}^{2+} + HY^{2-} \quad (4)$$

In Figure 4a, a small fraction of the initial absorbance signal decays until within ca. 200 μs a plateau is attained. The remaining MV^+ absorption is stable in the absence of catalyst or O_2. This fractional decay is attributed to the back electron transfer:

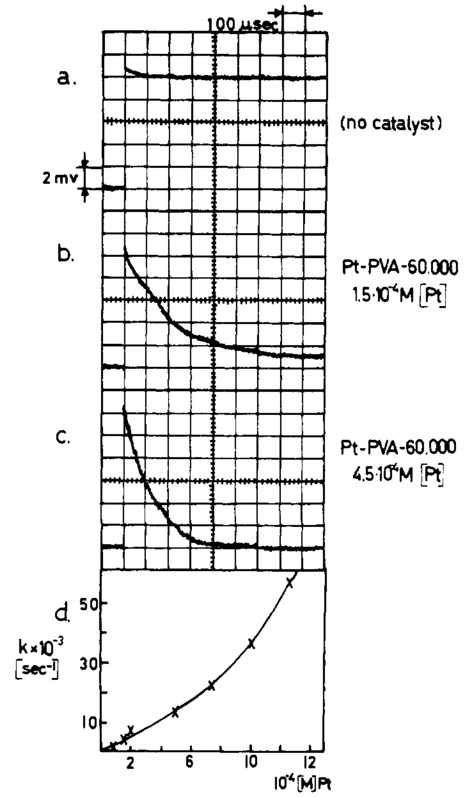


Figure 4. Effect of the Pt-PVA catalyst concentration on the behavior of MV^+ absorption at 600 nm. Representative oscilloscope traces are included in a, b, c. In d, the rate constants for MV^+ decay are plotted vs. platinum concentration of the Pt-PVA catalyst used (pH 5).

$$HY^{2-} + MV^+ \rightarrow MV^{2+} + HY^{3-} \quad (5)$$

which competes with deprotonation

$$HY^{2-} \rightarrow Y^{3-} + H^+ \quad (6)$$

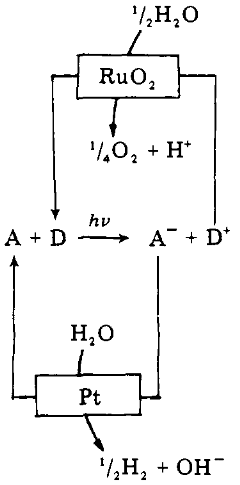
The radical ion Y^{3-} has reducing properties and hence cannot reoxidize MV^+.

In the presence of colloidal Pt (R_H = 110 Å), one observes an enhanced decay of the MV^+ absorption, Figure 4b,c. The signal returns now completely to the base line, the rate of the decay increasing sharply with Pt concentration. From a fitting of the absorbance decay curves to an exponential time law, one obtains the rate constants which are plotted as a function of Pt concentration in the lower part of Figure 4. The ascent of the curve is steeper than linear, indicating that the reaction order is greater than one with respect to the Pt concentration.

At a concentration of 10^{-4} M Pt in Pt-PVA polymer, we observe a rate constant $k = 0.14 \times 10^3$ s^{-1}. At the highest concentration of catalyst (12.5×10^{-4} M Pt content), the rate was 5.7×10^4 s^{-1}. The lifetimes observed for MV^+ were shortened from about 7000 to 15 μs, when the concentration of catalyst varied only by a factor of about 12. A rigorous theoretical treatment, using the differential reaction diffusion equation, is presently under way to explain these complex kinetic phenomena.

To obtain efficient recycling of MV^+ under steady-state illumination, it is necessary to employ a minimum Pt concentration which amounts to 0.5×10^{-4} M Pt. Evidently, such a Pt content is sufficient to reoxidize the MV^+ rapidly enough to avoid a significant buildup of MV^+ concentration. The same minimum amount of catalyst is required to induce an appreciable rate of H_2 production (see Figure 3).

These results are of general importance for the utilization of photo redox processes to split water into hydrogen and oxygen:



It appears that, by suitable choice of the catalyst, the conversion of A^- into A and simultaneous formation of hydrogen can be accomplished so rapidly that it can compete efficiently with the thermal back reaction. (In the photostationary state achieved under sunlight irradiation, the latter process, due to its bimolecular nature, should require at least several milliseconds). Moreover, redox catalysts such as colloidal RuO_2 have been shown[2] to mediate very effectively the back conversion of D^+ into D under simultaneous production of oxygen. Hence, in a mixture of RuO_2 and Pt colloids serving as selective microelectrodes for the A/A^- and D^+/D redox couples, light induced water splitting in a two-component system may become feasible. In fact, using $Ru(bpy)_3^{2+}$ as the photoactive donor and methyl viologen as the acceptor, cyclic water cleavage was recently observed in our laboratory under visible light illumination when a mixture of colloidal RuO_2 and Pt was used as redox catalysts.[2d]

(iv) Quantum Yield for Hydrogen Production. A crucial question which remains to be resolved is whether the electron transfer from MV^+ to the Pt particles

$$MV^+ + Pt \rightarrow MV^{2+} + Pt^- \qquad (7)$$

leads subsequently to stoichiometric formation of H_2 as expressed in eq 1. Figure 5 shows the growth of the MV^+ concentration in the absence of catalyst as a function of time of irradiation. The incident light was restricted in wavelength to 420–480 nm by means of a K-45 Balzers interference filter. The actinometry carried out here under the same conditions of illumination gave a value of 0.60×10^{17} quanta/min. The linear portion in Figure 5 gives a value $\phi(MV^+) = 0.30$ at irradiation times of less than 4 min. This compares favorably with $\phi(MV^+) = 0.15$-0.30 derived from laser photolysis experiments.[1c]

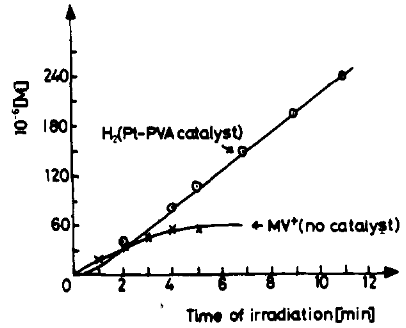


Figure 5. Dependence of MV^+ max formed on irradiation time using interference filter at 450 nm. Concomitant dependence of H_2 formed under the same conditions of illumination in the system: 4×10^{-5} M $Ru(bpy)_3^{2+}$, 2×10^{-3} M MV^{2+}, and 3×10^{-2} M EDTA at pH 5.

The H_2 yields show an induction period of up to 1 min. This may be due to the fact that sufficient MV^+ is not yet formed to subsequently generate H_2. Also, initially at very low levels of H_2 produced, the latter is retained in the liquid. After this period, the H_2 quantum yield remains at $\phi(H_2) = 0.13 \pm 10\%$ until the EDTA is consumed.

We conclude that, in the presence of suitable redox catalyst, hydrogen formation from water can occur rapidly and quantitatively, even if the driving force of the reaction—as in the case for MV^+—amounts to only several millivolts. These results encourage further work directed toward the utilization of colloidal systems in light energy conversion processes.

Acknowledgment. Acknowledgment is made to the Swiss National Foundation for supporting this work under Grant No. 4.061.076.04. We are also grateful to Ciba-Geiby Ltd., Basel, Switzerland, for financial aid. Thanks due to Miss Francine Duriaux for the preparation of the drawings.

References and Notes

(1) (a) G. V. Koryakin, T. S. Dzhabiev, and A. E. Shilov, *Dokl. Akad. Nauk SSSR*, **238**, 620 (1977); (b) J. M. Lehn and J. P. Sauvage, *Nouv. J. Chim.*, **1**, 449 (1977); (c) K. Kalyanasundaram, J. Kiwi, and M. Grätzel, *Helv. Chim. Acta*, **61**, 2720 (1978); (d) A. Moradpour, E. Amouyal, P. Keller, and H. Kagan, *Nouv. J. Chim.*, **2**, 547 (1978).
(2) (a) J. Kiwi and M. Grätzel, *Angew. Chem., Int. Ed. Engl.*, **17**, 860 (1978); (b) *ibid.*, **18**, 624 (1979); (c) *Chimia*, **33**, 289 (1979); (d) K. Kalyanasundaram and M. Grätzel, *Angew. Chem.*, **91**, 759 (1979); (e) J. M. Lehn, J. P. Sauvage, and R. Ziessel, *Nouv. J. Chim.*, **3**, 423 (1979).
(3) W. Pauli and E. Russer, *Kolloid-Z.*, **58**, 22 (1923).
(4) W. Dunworth and F. Nord, *Adv. Catal.*, **6**, 125 (1954).
(5) H. Thiele and H. S. von Levern, *J. Colloid Sci.*, **20**, 679 (1965).
(6) "Gmelin Handbuch", 8th ed., Teil A3, 1958, p 194.
(7) J. Turkevich, P. C. Stevenson, and J. Hillier, *Discuss. Faraday Soc.*, **11**, 55 (1951).
(8) R. Zsigmondy, *Z. Anal. Chem.*, **40**, 197 (1901).
(9) J. G. Calvert and J. N. Pitts, "Photochemistry", Wiley, New York, 1967, p 784.
(10) V. Degiorgio, in "Photon Correlation Spectroscopy and Velocimetry", H. Z. Cummins and E. R. Pike, Eds., Plenum Press, New York, 1977, p 142; M. Corti and V. Degiorgio, *Ann. Phys.*, **3**, 303 (1978).
(11) For exchange current densities and overvoltage of the H_2 evolution on Pt, see, for example: J. O. M. Bockris and S. Srinavasan, *Electrochim. Acta*, **9**, 71 (1964); H. Kita, *J. Electrochem. Soc.*, **113**, 1095 (1966); S. Schuldiner, T. Warner, and B. Piersma, *J. Electrochem. Soc.*, **114**, 343 (1967).