

Notes

Photochemical Investigations of Ce(III)-V(V) System in Glasses

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Ce(III)-V(V) system in glasses is photosensitive and the electrons loosened from Ce(III) by the UV light are trapped in the vacant sites provided by the irregular five-coordinate VO_3^- ion. The trapped electrons form metastable colour centres which absorb around 19230 cm^{-1} and are independent of the oxidation states of vanadium in the photoredox process.

CONSIDERABLE interest has been assigned in the photosensitivity of glasses containing cerium oxide alongwith transition and non-transition metal oxides¹⁻⁴. Löffler⁵ and Weyl⁶ investigated V_2O_5 - Ce_2O_3 couple while Kumar and Sen⁷ studied the optical spectra of the solarized Mn(III) and V(II) in glasses and claimed the photoreduction of V(III) to V(II). Since there is no previous report on the preparation of photosensitive glass containing Ce(III)-V(V) system under oxidizing conditions, the preparation and spectral study of such a glass has been undertaken because Ce(III)-V(V) system should be even more susceptible to photooxidation-reduction than Ce(III)-V(III) due to the presence of V(V) which is a stronger electron acceptor than V(III).

Preparation of the glass — All the chemicals used were of BDH (AR) quality. In a base glass containing (wt %) Na_2O 18, MgO 8, and SiO_2 74, CeO_2 0.30% and V_2O_5 0.15% were added. NaNO_3 (5%) was introduced to keep the oxidizing atmosphere in the melt. The batch was thoroughly mixed and melted for 4 hr in a Pt-Rh crucible in an electric furnace at 1450° . The molten glass was poured, cooled, crushed and remelted for another 2 hr for attaining maximum homogeneity. Finally, the molten glass was cast in a mould and annealed at 560° . It was then cut into pieces, ground and polished up to 2 mm thickness. The glass pieces were exposed to UV radiations from a 'Votan' high pressure mercury lamp at a distance of 9 inches for 1 or 2 hr each with and without blue filter. Both the surfaces of the glass pieces were uniformly exposed to the UV radiations. Absorption spectra of the non-irradiated and the radiated glass pieces were recorded on a Cary 14 model in the 300-750 μ range.

Since the above glass containing Ce(III)-V(V) has been prepared under strongly oxidizing conditions, it was colourless, transparent, strongly absorbing in the UV region but showing no absorption in the

visible region. It, therefore, contained V(V) which is either colourless or faintly yellow because of the absence of electrons in the d -level. When the glass was subjected to the UV radiations it turned purple. Besides showing a strong absorption in the UV region, it showed a distinct absorption band at 19230 cm^{-1} in the visible region, the intensity of which increased with increasing duration of exposure without any change in wavelength.

In solution, stepwise reduction from V(V) to V(II) takes place with mild to strong reducing agents and the various oxidation states can be stabilized in complexes^{8,9} or crystals^{10,11}. In glasses, however, such conversions from higher to lower oxidation states are a matter of controversy because it is a solid rigid lattice. Photoreduction of vanadium is even more complicated to explain because of the simultaneous existence¹² of V(III), V(IV), V(V) or V(IV), V(V). Although, Kumar and Sen⁷ claimed to have photoreduced V(III) to V(II) in Ce(III)-V(III) system but the authors failed to satisfactorily explain the development of a new band at 19230 cm^{-1} which is at much shorter wavelength as compared to the one 17850 cm^{-1} band in the hydrated crystals of V(II). Moreover, the photo-reduced V(II) in glass does not show another band at 12190 cm^{-1} observed in the hydrated crystals^{10,11}. When the purple colour and the absorption bands of the photoreduced glass containing Ce(III)-V(III) system are compared with the photoreduced glass containing Ce(III)-V(V) system, marked similarity of the colour and absorption bands are observed. V(II) species cannot be present in Ce(III)-V(V) system because in a photochemical reaction, the electron donor species give one electron at a time. Even the light radiations excite only one electron so that the UV light must have excited only one electron in the Ce(III)-V(V) system. Moreover, the ratio of Ce(III) to V(V) in the glass is 2:1 in the present case. Even if it is assumed that all the Ce(III) ions lose one electron each and all the electrons are transferred to V(V) ions, the V(V) ions should first be reduced to V(IV) and then to V(III) state. All attempts to observe such a behaviour have failed. Further, the behaviour of the photoreduced glass towards heat treatment is similar to that in metastable V(II) developed from V(III). In metastable V(II), the colour changes from green to red-violet on photoreduction. By heating the glass to 250 - 300° , the loose electrons return to the Ce(IV) ion with a simultaneous return to the green colour of V(III) and emission of a quantum of light¹³. The original colour of the glass, in the present case, is also restored on heating around 400°C . This observation confirms the presence of metastable V(IV) or $[\text{V(V)}+e]$ in the Ce(III)-V(V) glass.

In $\text{KVO}_3 \cdot \text{H}_2\text{O}$ and V_2O_5 , the vanadium ions have irregular type of five-coordination which is trigonal bipyramidal¹⁴. In glasses cerium(III) vanadate^{+e}

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(CeVO₄) may provide several vacant sites which on photoexcitation are occupied by the electrons. The trapped electrons, thus held up in the state of suspension by strongly electronegative oxide ions surrounding the V(V), are not able to reach the *d*-levels of vanadium(V) and, therefore, do not cause the reduction of V(V) to V(IV). Further, with increasing duration of exposure, the increase in the intensity of the 19230 cm⁻¹ band, is another evidence of the trapped electrons rather than the photoreduction of V(V) to V(IV). Thermal agitation reverses the direction of electron mobility and the electrons are regained by Ce(IV), consequently, restoring the original colour of the glass.

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Calculation of π -Electronic Spectra of Benzonitrile, Nitrobenzene, Dinitrobenzenes & Nitrophenols

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The π -electronic spectra of benzonitrile, nitrobenzene, dinitrobenzenes and nitrophenols have been calculated using Molecules in Molecules method. The two-centre repulsion integrals are calculated by the Nishimoto-Mataga approximation. The values of the resonance integrals are considered as adjustable parameters. The direct charge transfer energies and the effect of hydrogen bond have been taken into consideration in case of nitrophenols. The calculated spectral transition energies are in good agreement with the experimental ones. Starting parameters are suggested for MIM calculations of compounds having nitro, cyano, hydroxy groups.

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THE π -electronic spectra of benzonitrile, nitrobenzene, dinitrobenzenes and nitrophenols were calculated by the Molecules in Molecules (MIM) method. The two-centre repulsion integrals were calculated by the Nishimoto-Mataga approximation¹ in preference to the other methods²⁻⁴. The $\beta_{\mu\nu}$ resonance integrals were taken as variable parameters. The nitro and cyano groups were taken as acceptors and the hydroxy group as donor compared to the benzene ring.

The various experimental and theoretical⁵ parameters, bond distances ($r_{\mu\nu}$), valence state ionization potentials (I_{μ}) and electron affinities (A_{μ}), one-centre repulsion integrals ($\gamma_{\mu\mu}$) needed for the calculation are given in Table 1. The locally excited configurations of the subsystems were calculated by the PPP type SCF calculations using the above data as well as $\beta_{C\equiv N} = -3.5$ eV and $\beta_{NO} = -3.0$ eV for resonance integrals (values found as the best for benzonitrile and nitrobenzene). The calculated wave functions (ψ) and the experimental π -electron transition energies of the subsystems, nitromethane and acetonitrile are given below, where α_i denote the atomic orbitals. CH₃NO₂; ($E_{\text{expl}} = 6.2616$ eV)^{3,6}; $\psi_1 = \alpha_2^{-1}\alpha_3$; $\psi_2 = \alpha_1^{-1}\alpha_3$. $\alpha_1 = 0.7297\alpha_1 + 0.4835(\alpha_2 + \alpha_3)$; $\alpha_2 = 0.7071(-\alpha_2 + \alpha_3)$; and $\alpha_3 = 0.6838\alpha_1 - 0.5160(\alpha_2 + \alpha_3)$. CH₃CN; ($E_{\text{expl}} = 7.4240$ eV)^{3,6}; $\psi = \alpha_1^{-1}\alpha_2$. $\alpha_1 = 0.6415\alpha_1 + 0.7671\alpha_2$; and $\alpha_2 = 0.7671\alpha_2 - 0.6415\alpha_1$.

The locally excited configurations and electron transitions of benzene ring were taken from our earlier work⁷. The experimental ionization potentials of donor subsystems are: $I_{\text{benzene}} = 9.245$ eV⁸, $I_{\text{CH}_3\text{OH}} = 10.83$ eV⁹. The experimental electron affinity of acceptor subsystems are: $A_{\text{benzene}} = -1.10$ eV¹⁰, $A_{\text{CH}_3\text{NO}_2} = -0.56$ eV¹¹.

There is lack of experimental electron affinity data on benzonitrile. Therefore this parameter had to be taken as a variable parameter together with the resonance integral β_{C-CN} . The results are shown in Fig. 1, where the horizontal lines represent the experimental energies. The differences between the two β_{C-CN} values giving the two exact energies are drawn in the upper part of the Fig. 1. The results show that calculations carried out with larger electron affinities give better results. On the other hand considering the cyano group as an acceptor the upper limit of its electron affinity seems to be that of benzene ring (-1.10 eV). For this reason, the electron affinity of acetonitrile was taken as $A_{\text{CH}_3\text{CN}} = -1.00$ eV, corresponding to an optimum value of $\beta_{C-CN} = -2.5$ eV.

TABLE 1 — CALCULATED ATOMIC PARAMETERS AND EXPERIMENTAL BOND DISTANCES

μ	I_{μ} (eV)	A_{μ} (eV)	$\gamma_{\mu\mu}$ (eV)	$r_{\mu\mu}$ (Å)*
C (<i>trivtr</i> π)	11.16	0.03	11.13	1.397
N (<i>trivtr</i> π^2 ; nitroi)	25.73	8.97	16.76	1.46
O (<i>trivtr</i> π ; nitroi)	17.70	2.47	15.23	1.21†
C (<i>di</i> $\pi\pi$; cyanoi)	11.19	0.10	11.09	1.455
N (<i>di</i> $\pi\pi$; cyanoi)	14.18	1.66	12.52	2.614
O (<i>trivtr</i> π^2 ; hydroxyi)	30.07	10.83	19.24	1.36

*Obtained from ref. 14-16.

†NO.