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Nano-porous TiO_2 photovoltaic cells sensitized with metallochromic triphenylmethane dyes: [n-TiO_2/triphenylmethane dye/p-I^-/I_3^- (or CuI)]

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Abstract

Photovoltaic cells capable of generating high photo-current densities and voltages were fabricated using metallochromic triphenylmethane type dye materials by depositing nano-porous TiO_2 films onto a thin film of SnO_2 coated conducting glass. Two dye materials belonging to the triphenylmethane class namely, bromopyrogallol red and pyrocatechol violet were investigated. Molecular orbital calculations and contour plot have indicated that the LUMO level is localized on the Ti(IV) ion, whereas the HOMO level is centered around the ligand. Moving from wet cell, i.e. using I^-/I_3^- as the redox mediator to p-type solid semiconductor CuI reduces the photo-current conversion efficiency approx. 38%. Good stability for photo-current and photo-voltage were noticed when the incident light path was intercepted using UV and IR filters. Scanning electron microscopic data have revealed that particle sizes are in the range of 50–100 nm for the CuI and 10–25 nm for the deposited colloidal TiO_2 respectively. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Dye sensitization; Photochemical cells; Titanium dioxide; Bromopyrogallol red; Pyrocatechol violet

1. Introduction

Considerable interest is still on for the development of a stable and relatively low cost dye-sensitized photovoltaic cell to harness the solar energy. Dye sensitization process has been widely used in conjunction with wet electrodes, where the photoelectrochemical cell is made by depositing dye material onto a conducting glass plate coated with nano-porous high band gap semiconductors like TiO_2 and with a suitable liquid redox couple (e.g. I^-/I_3^-). However, there are several disadvantages when using wet photoelectrochemical cells such as dye desorption, solvent evaporation due to seal imperfections etc. The development of dye sensitized nano-porous solid state devices [1] by replacing the liquid electrolyte with CuI or CuCNS p-type semiconductors have overcome some major technological difficulties.

Nevertheless, main problem that scientists still face is their low efficiency of photo-current conversion and particularly photodegradation of the dye material. Ruthenium polypyridyl dyes have shown fairly high photo-current conversions, ca. 10% and with a reasonable stability. However, these inorganic dye materials are comparatively expensive when considering the synthesis process involves [2]. Carboxylic functional groups attached to the polypyridyl ligand acts as anchors by chelating with surface hydroxyl groups of colloidal TiO_2. Photophyscial and photochemical aspects of most of these ruthenium dyes have been well characterized by several workers [3] by ultrafast flashphotolysis and spectroscopic techniques. This paper reports the results obtained using two structurally similar dye materials having triphenylmethane central frame. Structures of the two triphenylmethane dyes are shown in Fig. 1. Construction of typical liquid and solid state photocells are shown in Fig. 2. Supplementary computational data and scanning electron microscopic data are also discussed.

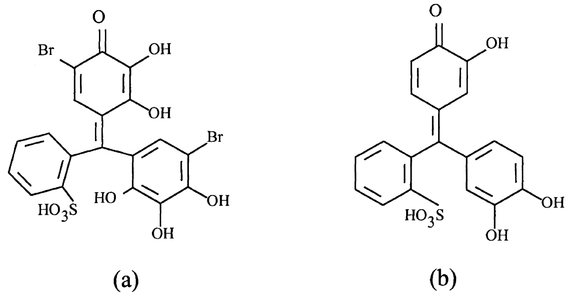

Fig. 1. (a) Bromopyrogallol red (b) Pyrocatechol violet.

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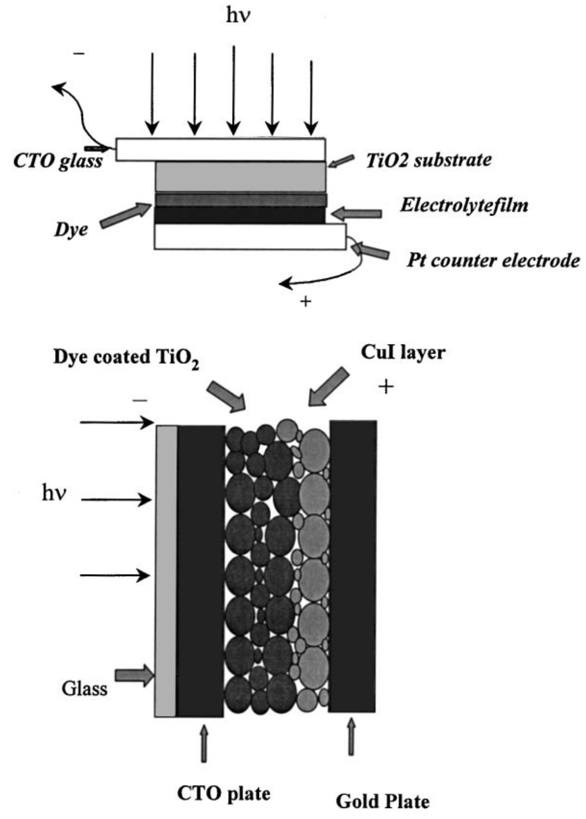


Fig. 2. Construction of dye sensitized solid state solar cell.

Table 1
Average photo-current and voltage values of wet cell (AM1 solar simulator). Values in brackets are when the cell is exposed to normal sun light

Dye	Photo-current (mA cm^{-2})	Photo-voltage (mV)
Bromopyrogallol red	4.7 (5.3)	478 (513)
Pyrocatechol violet	1.6 (0.9)	245 (318)

Table 2
Average photo-current and voltage values of dry cell (AM1 solar simulator). Values in brackets are when the cell is exposed to normal sun light

Dye	Photo-current (mA cm^{-2})	Photo-voltage (mV)
Bromopyrogallol red	1.8 (2.5)	345 (408)
Pyrocatechol violet	0.36 (0.3)	56 (88)

2. Experimental

Nano-porous layers of TiO_2 were coated on CTO glass (1 cm × 2 cm, sheet resistance approx. 17 $\Omega\,cm^{-2}$) by previously described method [4] using colloidal suspension of TiO_2. Ground state absorption spectra of the pigments in water were recorded using Shimadzu (UV-3000) double beam spectrophotometer. Photo-current action spectra (i.e. dependency of the observed photo-current with the function of wavelength) were monitored using Nikon monochromator Auto-scanner AS-C 101 equipped with Stanford Research lock-in-amplifier.

TiO_2 plates were coated with dye material by warming them in an aqueous solution containing 0.1 M $NaNO_3$ It has been found that $NaNO_3$ improves [5] the solubility of dye in water which also prevents the formation of dye molecules aggregation on nanoporous TiO_2 and further it enhances the formation of dye monolayers on the adsorbate. Liquid state photovoltaic cells (‘Greatzel’ type) were fabricated by sandwiching a film of electrolyte containing ethylene carbonate, acetonitrile (8 : 2 by weight), 0.5 M tetrapropyl ammonium iodide and 0.05 M I_2 in between dyed coated TiO_2 plate and Pt islet deposited conducting SnO_2 glass. Pt coated surface on SnO_2 was prepared either by thermal evaporation or cathodically electrolyzing a solution of hexachloro-platinic acid. In order to tailor fully solid state cell in which liquid electrolyte is now being replaced by a hole-conducting CuI semiconductor was deposited on the dye-coated porous surface by coating from a solution of CuI in acetonitrile at an elevated temperature. Electrical contact was made by pressing a gold-coated CTO glass onto the CuI surface.

Molecular modeling and computational calculations were carried out using an IBM compatible PC with HyperChem [6] software. Scanning electron microscopic data were obtained from JSM-330 JEOL SEM.

3. Results and discussion

The metallochromic triphenylmethane dye materials have been successfully used by several research workers in trace metal analysis using its powerful chelating ability with number of transition metal ions [7,8]. Such complexes show fairly high molar extinction coefficients in the visible absorption region. In the case of TiO_2 coordinated systems visible absorption band shows a red shift and a similar behavior has been observed [2] for the $[Ru(dcbyp)_3]^{2+}$ where, dcbpy = 2,2′-bipyridyl 4,4′ dicaboxylaic acid. This effect was attributed to the reduction of electron donating strength of O atoms upon chelation with TiO_2 particles.

Average values of open-circuit voltages **(I_{ov})** and short-circuit currents (I_{sc}) for the two dye materials obtained in the form of wet cell, i.e. using $I^-/I_3{}^-$ under AM1 solar illumination and typical afternoon sunlight are given in Table 1. Values obtained in the form of solid state (or dry) cells, i.e. using CuI as the p-type hole acceptor, are given in Table 2. It is clear from these data that moving from ‘wet-cell’ to ‘dry-cell’ causes a slight reduction of open-circuit voltage and short-circuit current. The reduction may have been caused by the increase in internal resistant and fairly large particle size of the CuI layer, approximately 50–100 nm. As a result, photo-current conversion efficiency of fully solid state photocell has dropped to approx. 38% than its corresponding wet cell.

Ground state absorption and photo-current action spectra of the two dye materials are shown in Figs. 3 and 4. Photo-current action spectra of the two dye materials are broad and centered around 585 nm and 560 nm for bromopy-

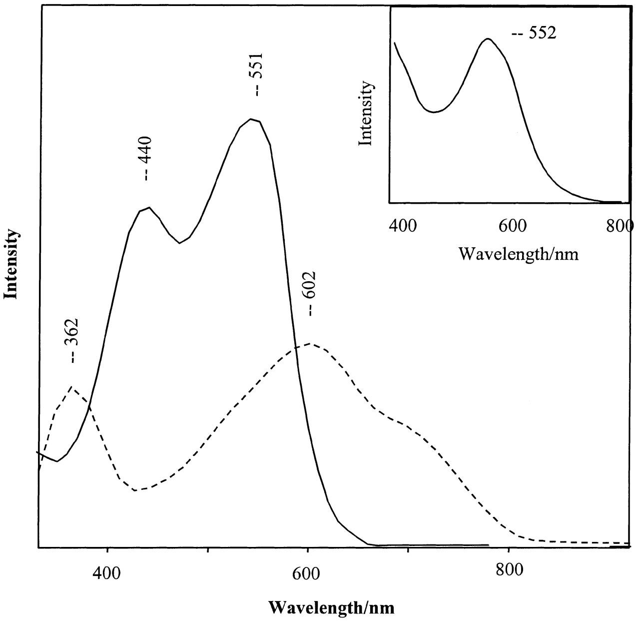


Fig. 3. Aqueous medium absorption (—) and photo-current action (--) spectra of bromopyrogallol red sensitized cell. Inserted, aqueous medium absorption spectrum in the presence of colloidal TiO_2.

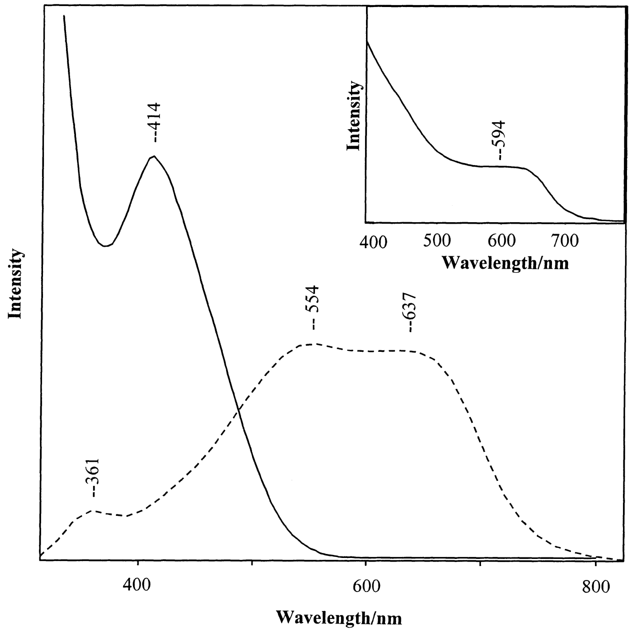


Fig. 4. Aqueous medium absorption (—) and photo-current action (--) spectra of pyrocatechol violet sensitized cell. Inserted, aqueous medium absorption spectrum in the presence of colloidal TiO_2.

Table 3
Photo-current conversion efficiencies of fabricated cells

Dye	Photo-current conversion efficiency (dry cell)	Photo-current conversion efficiency (wet cell)
Bromopyrogallol red	0.23%	0.6%
Pyrocatechol violet	–	0.1%

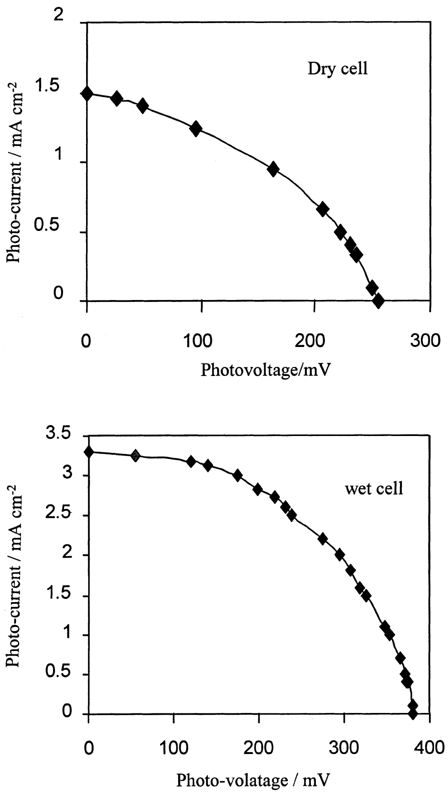


Fig. 5. Current–voltage curve for illuminated bromopyrogallol red sensitized TiO_2 films, a) for wet cell, b) for dry cell. The *I–V* curves were measured using a 10 KΩ maximum variable load while the cell was illuminated by full sun.

rogallol red and pyrocatechol violet sensitized cells respectively. Comparison of the two absorption spectra shows that for the bromopyrogallol red, absorption band maximum centered around 551 nm is more intense and its tail extends up to 650 nm. In contrast, absorption band maximum for the pyrocatechol violet band at visible region with its tail extending only up to 550 nm is of much weaker intensity. Hence, bromopyrogallol red is much more effective than pyrocatechol violet for the harnessing solar energy.

Calculated photo-current conversion efficiencies are given in Table 3. Photo-current conversion efficiency of pyrocatechol violet sensitize solid state was unable to obtain due its low output. Fig. 5 shows the *I–V* curves of bromopyrogallol red when used as solid and wet cells. The two dye molecules which belongs to the triphenylmethane class having a common central main frame have produced different cell efficiencies and current-voltage properties. One possible explanation for this is that bromopyrogallol red can harvest photons having energies well into the near infrared side of the spectrum than pyrocatechol violet. The differences between calculated binding energy and heat of formations of bromopyrogallol red and pyrocatechol violet with TiO_2 are about 8065 kcal mol^{-1} and 236 kcal mol^{-1} respectively. Therefore, it is evident that bromopyrogallol dye strongly chelate with Ti^{4+} ion than pyrocatechol violet with the hydroquinoe moiety of the ligand. In addition, bromopyrogal-

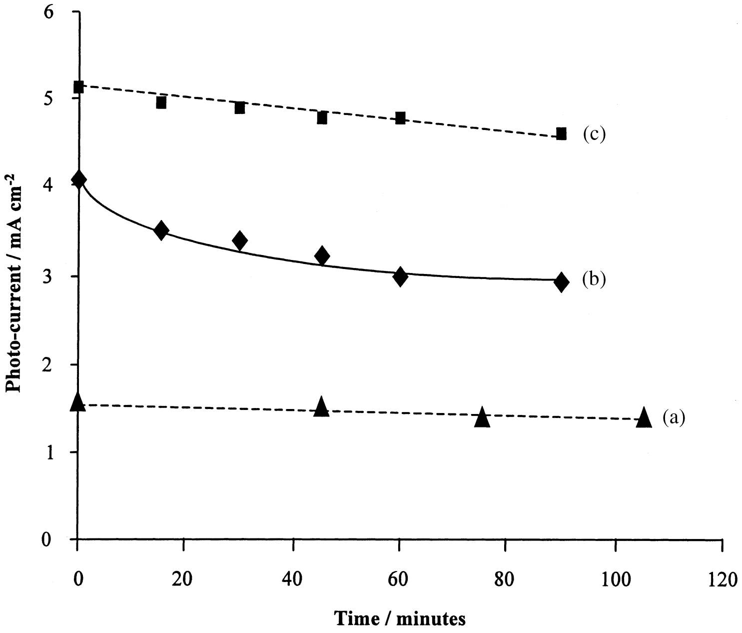


Fig. 6. The time development of the photo-current when bromopyrogallol red sensitized wet cell was illuminated with the AM1 solar simulator, a) in the presence of UV filter, 1 M $NaNO_3$ solution was used as a filter. b) without a UV filter, c) with IR filter.

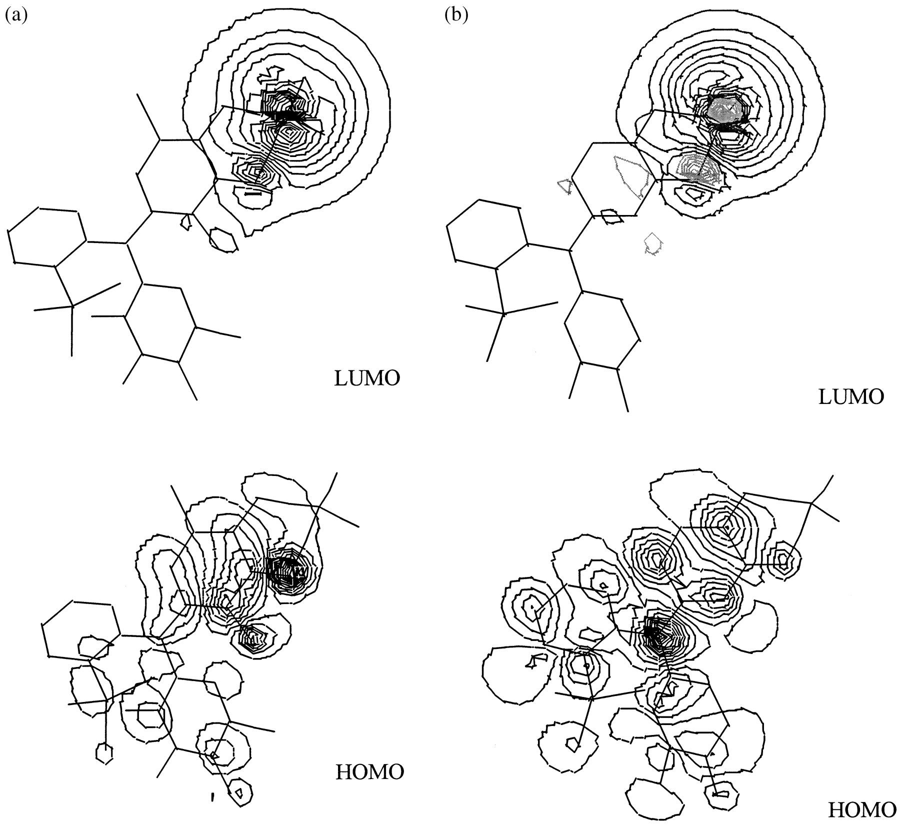


Fig. 7. Contour plots of HOMO and LUMO levels of Ti(IV) chelated bromo pyrogallol red ligand, (a) and pyrocatechol violet, (b).

lol red has several −OH groups that could act as potential anchoring sites with TiO_2 surface and allowing charge transfer process to occur from different sites of the molecule.

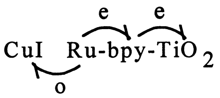
Stability of the output photo-current and voltage can be improved by avoiding oxygen and moisture during the construction of cells, particularly when coating CuI layer. Increased porosity due to lager particle size could easily trap moisture and oxygen present in the atmosphere. Coating of CuI layer under an inert atmosphere have shown enhanced stability of observed current-voltage properties. Further, by blocking UV and IR radiation, stability of the cell output can be improved (Fig. 6). Photodegradation mechanisms under various experimental conditions have been previously reported by us [9].

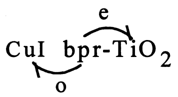
Molecular modeling studies of the dye molecules have indicated that torsion angle between hyrdoquionone containing ring and $-SO_3^-$ group containing ring is about 35.5° and 24.2° for the bromopyrogallol red and pyrocatechol violet respectively. However, the angle between hyrdoquionone containing ring and the other ring is only about 12° for both the molecules. Slight increase in torsion angle of bromopyrogallol red may have been caused by the bulky −OH substituents groups attached in the adjacent ring. For the unsubstitued triphenylmethane molecule these angles are about 57.5°. This confirms that torsion angle is strongly affected by the substituents groups attached to the three rings and the two dye molecules are not geometrically identical. Contour plots obtained for the coordinated systems from ZINDO/l semi-empirical calculation are shown in Fig. 7. For both molecules, LUMOs electron densities are localized on the metal center, whereas, HOMOs are localized mainly on the ligand. This confirms the charge transfer nature of the dye TiO_2 the coordinated systems.

These calculations were based on optimizing the geometry initially by MM+ method and subsequently by AM1 [10] [1] or ZINDO/l [11] [2] semi-imperial calculation methods using HyperChem computation software.

4. Conclusion

Two dye materials, bromopyrogallol red and pyrocatechol violet having a common central frame show current voltage properties when used as sensitzer in nano-pourous photocells. Photocurrent conversion efficiencies show significant difference for the two dye materials. Comparison of ground state absorption spectra of the two dye materials indicate that bromopyrogallol red is much more effective in harnessing solar energy than pyrocatechol violet. However, obtained current–voltage properties are lower than the that of the cells constructed with ruthenium based bipyridyl complexes [12]. The difference is that the nature of charge transfer excitation, where in the ruthenium based bipyridyl complexes excitation involves MLCT (metal-to-ligand charge transfer) process. It is a well establish fact that excited photo electron is localized on one bipyridyl ligand [13,14] and hence subsequent electron injection occurring from a electron localized anti-bonding orbital of bipyridyl ligand to the CB of the TiO_2. On the other hand dye materials like bromopyrogallol red and pyrocatechol violet, ligand centered excitation (S/S*) is responsible for the charge injection. It is clear the that back electron transfer process is much favorable in organic dye molecules chelated to TiO_2 the surface than organometallic complexes where electron injection occurring from a charge transfer excitation process.





Although any solar cell device from these two dye materials are not practically and commercially possible, understanding the properties required from a molecular point of view help us to design a solar cell based on dye sensitization process having high photo-current conversions efficiency with an excellent photo-stability.

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References

[1] K. Tennakone, G.R.R.A. Kumara, A.R. Kumarasinghe, K.G.U. Wijayantha, P.M. Sirimanne, Semicond. Sci. Technol. 10 (1995) 1689.
[2] M.K. Nazeeruddin, A. Key, I. Rodicao, R. Humpry-Backer, E. Muller, P. Liska, N. Vlacopoulas, M. Graeatzel, J. Am. Chem. Soc. 115 (1993) 6382.
[3] Nerine. J. Cherephy, Greg. P. Smested, Micheal Graeatzel, Jin Z Zhang, J. Phy. Chem. B 101 (1997) 9342.
[4] K. Tennakone, G.R.R.A. Kumara, K.G.U. Wijayantha, I.R.M. Kottegoda, V.S.P. Perera, G.L.M. Aponsu, J. Photochem. Photobiol. A. Chem. 108 (1997) 175.
[5] I. Nemcova, L. Cermacova, Collection of Czechoslovak Chemical Communications 52 (1992) 1658.
[6] HyperChem, Release 4.5, Hypercube.
[7] D.T. Bums, D. Dadger, Analyst 105 (1980) 1082.
[8] Z. Hausenblasova, I. Nemcova, V. Suk, Microchem. J. 26 (1981) 262.
[9] K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, K.G.U. Wijayantha, Semicond. Sci. Technol. 12 (1997) 128.
[10] M.J.S. Dewar, E.G. Zoebisch, E.F. Healy, J.J.P. Stewart, J. Am. Chem. Soc. 107 (1985) 3902.
[11] M.C. Zerner, Inorg. Chem. 28 (1986) 2728.
[12] K. Tennakone, G.R.R.A. Kumara, I.R.M. Kottegoda, K.G.U. Wijayantha, V.P.S. Perera, J. Phys. D: Appl. Phys. 31 (1998) 1492.
[13] W.H. Woodward, R.E. Dallinger, M.Z. Hoffman, P.G. Bradley, D. Presser, V. Malueg, R.J. Kessler, K.A. Norton, Time-Resolved Vibrational Spectroscopy, Academic Press, 1983, p. 147.
[14] C.G. Coates, T.E. Keyes, J.J. McGarvey, H.P. Hughes, J.G. Vos, P.M. Jayaweera, Coord. Chem. Rev. 171 (1998) 323.

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[1] AMl (Austin Model 1).

[2] ZINDO/1 and ZINDO/S (Zerner's intermediate neglect of differential overlap).