

COMMENTS

Comment on “Photoluminescence Study of the Introduction of V in Si-MCM-41: Role of Surface Defects and Their Associated SiO[−] and SiOH Groups”

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A recent paper by Dzwigaj et al. (*J. Phys. Chem. B* 2003, 107, 3856) employs photoluminescence spectroscopy to characterize a novel series of vanadium-doped MCM-41 materials initially developed by one of the authors.¹ There are two major conclusions drawn from the analyses of these spectra. The first is that the vibrational fine structure observed in the emission is in mode characteristic of the terminal V=O stretch on pseudotetrahedral vanadium, which, in turn, identifies this site in the material. The second is that an observed blue luminescence (~470 nm) originates from Si—O[−] and Si—OH defect sites, which are consumed (quenched) by the vanadium incorporation. In our view this study is highly flawed and, though some of the conclusions may be coincidentally correct, they are not supported by the data presented due to flaws in the analysis and interpretation of the spectroscopic data.

In their analysis, the vibrational mode in the emission spectrum of vanadium in silica is assigned to the terminal V=O stretch of the C_{3v} pseudotetrahedral oxovanadium site, which occurs at 1042 cm^{−1}. Figure 1a is the 77 K vanadium luminescence spectrum, obtained at 305 nm excitation, which was scanned and digitized from Figure 4c of ref 1 (sample C-14, 1.1% V). To support this assignment, the authors assert that differences between 0–0 and 0–1 modes, as determined from minima in the second derivative of the emission spectrum, are in good agreement with the 1042 cm^{−1} value. In fact, without the benefit of resolved absorption or emission excitation spectra, the placement of the E₀₀ in the baseline at ~410 nm is problematic because the first truly resolved mode occurs at ~430 nm. More importantly, the author's 0–0, 0–1, and 0–2 modes all appear as shoulders with no resolvable peaks and, contrary to their assertion, plotting first or second derivatives does not change this fact nor does it improve the analysis. As a result, the calculated differences between peak maxima can cover a wide range of values depending on where peak maxima are assigned. In effect, the authors have selected the weakest, most poorly resolved modes to support their assignment of a 1042 cm^{−1} active mode. In fact, if differences between the well-resolved 0–3 to 0–7 modes are determined using their methodology, an average value of 990 cm^{−1} is obtained from their spectra.

Historically, analysis of vibronic structure in electronic spectra is usually carried out using well-established analytical expressions for the Franck–Condon overlap integral in the harmonic approximation. This approach typically involves simulating the spectrum as a stick diagram that reproduces the frequency of the progression and the relative intensities of the modes.²

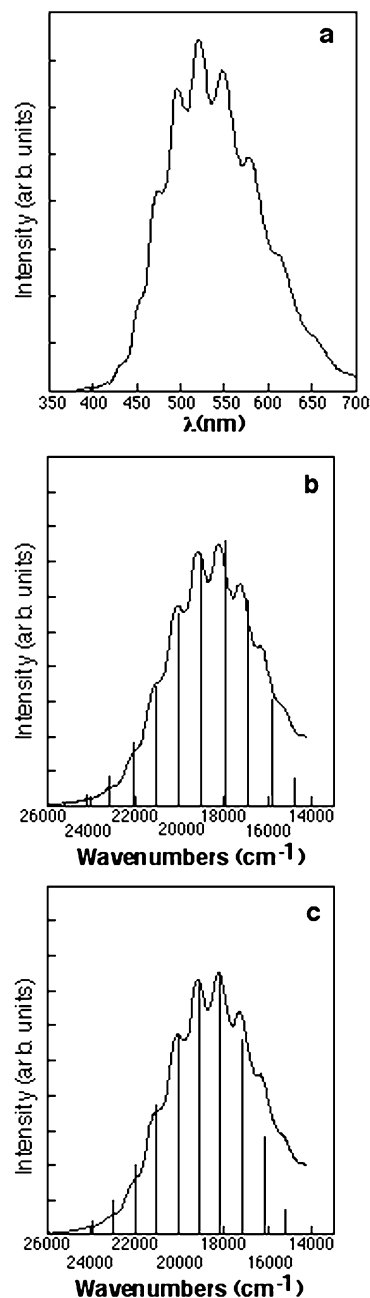


Figure 1. Photoemission from vanadium sites in 1.1% V in Si-MCM-41 (305 nm excitation; 77 K, from ref 1, Figure 4c): (a) showing resolved vibrational progressions; (b) after correction for nonconstancy in the band-pass with calculated Franck–Condon progression for $\nu = 1042$ cm^{−1} and $E_{00} = 24\,186$ cm^{−1} ($\mu = 16$ amu (O), $S = 0.137$); (c) with calculated Franck–Condon progression for $\nu = 970$ cm^{−1} and $E_{00} = 22\,970$ cm^{−1} ($\mu = 67$ amu (O+V), $S = 0.070$). Calculations based on equations in ref 2d.

Parameters input into such an analysis are the zero-point energy (E_{00}), the frequency of the progression (ν), the reduced mass (μ) of the active mode, and the normal coordinate change (S), with the latter two parameters affecting the relative intensities of the modes. Though more sophisticated analysis has subse-

quently been developed, this approach gives very good agreement with the experimental data, especially for relatively simple single-mode progressions such as exhibited by vanadia bound to silica.³ To analyze a vibronic progression, the spectra need to be plotted in energy units (usually cm^{-1}). When spectra are recorded, as these have, with constant wavelength resolution, this cannot be correctly accomplished by simply inverting the wavelength scale as the authors have apparently done. Instead, the spectra must be correct by multiplying the intensity by a factor of the wavelength squared ($I(\nu) = \lambda^2 I(l)$) to compensate for nonconstancy in the band-pass.⁴ This is a well-known and necessary correction, especially in broad emission bands such as these. The effect of this correction is to increase the intensity of the long wavelength side of the spectrum, which will shift the positions of the vibronic bands and change their relative intensities. Figure 1b shows the emission spectrum from the cited article plotted in cm^{-1} with the appropriate correction applied.

Figure 1b also shows the results of a Franck–Condon analysis of the spectrum using their value for E_{00} ($24\,186\text{ cm}^{-1}$), taken from the second derivative spectrum (C14; Figure 5) and a 1042 cm^{-1} mode representing the terminal $\text{V}=\text{O}$ stretch. As can be seen, this mode is clearly too high in energy to adequately replicate the spectrum. Further, the relative intensities cannot be fit well with this mode and require an abnormally large normal coordinate change (0.137 \AA) in the best approximation. Consistent with our prior analysis of an analogous system, a mode of 970 cm^{-1} starting from an E_{00} of $23\,940\text{ cm}^{-1}$ replicates extremely well the total progression with some anharmonicity observed in the last three modes.⁵ This frequency corresponds to a bridging $\text{Si}-\text{O}-\text{V}$ stretch of the basal plane oxygen, which has been assigned both by us, on the basis of Raman studies and, unambiguously, by Scott using site selective isotopic labeling.⁶ Notably, the relative intensities are well fit by this mode and yield a more reasonable value for the normal coordinate change (0.070 \AA).

Finally, the authors assign the high-energy emission at around 470 nm to defect sites in the silica associated with SiO^- and SiOH groups in the silica. This assignment comes from a comparison to prior studies reporting luminescence spectra from oxidized nanocrystalline silicon.⁷ In our experience, the condition under which the materials have been treated (outgassed at 473 K at 10^{-3} Torr) is woefully inadequate to achieve reproducible emission spectra.⁸ Notwithstanding this, emission in this region is ubiquitous in silica materials derived from silica gel and sol–gel reagents such as silicon alkoxides and originates in large part from impurities (primarily Sn and Ge), which are

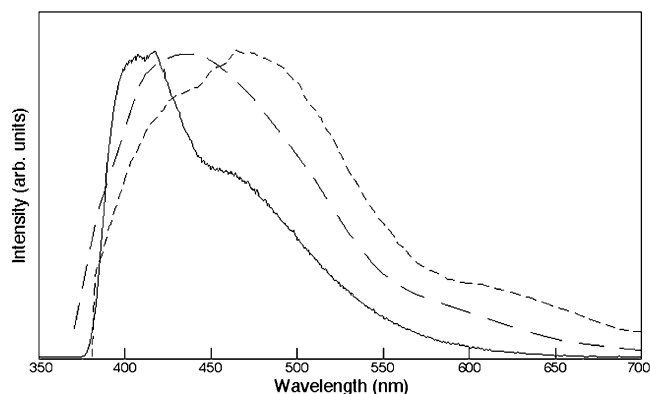


Figure 2. Photoemission of (—) Si-MCM-41 (250 nm excitation, 77 K; from ref 1, Figure 1B), of (---) OH-related centers in dispersed SiO_2 (340 nm excitation, RT, from ref 7, Figure 2a; reproduced with permission of Elsevier (copyright 1995)), and of (- · -) 0.1 mol % Sn in silica (280 nm excitation, 10 K).

always present.⁹ Figure 2 shows the emission spectrum reported by Dzwigaj (taken from Figure 1b, ref 1) overlaid with OH-related emission from finely divided silica (from Figure 2a, ref 7) and 0.1% Sn in silica. Obviously, neither the OH nor the Sn emission unambiguously reproduces the spectrum observed by the authors. Clearly their spectrum may well contain components of both of these emission sources or from other emissive sites. Regardless, the claim of hydroxyl consumption by vanadium incorporation is poorly supported by the photoemission evidence.

References and Notes

- (1) Dzwigaj, S.; Krafft, J.-M.; Che, M.; Lim, S.; Haller, G. L. *J. Phys. Chem. B* **2003**, *107*, 3856.
- (2) (a) Ballhausen, C. J. *Molecular Electronic Structures of Transition Metal Complexes*; McGraw-Hill: New York, 1979; p 125. (b) Yersin, H.; Otto, H.; Zink, J. I.; Gliemann, G. *J. Am. Chem. Soc.* **1980**, *102*, 951. (c) Ansbacher, F. Z. *Naturforsch.* **1959**, *14a*, 889. (d) McCoy, E. F.; Ross, I. G. *Aust. J. Chem.* **1962**, *15*, 573.
- (3) Zink, J. I.; Shin, K. S. *Adv. Photochem.* **1991**, *16*, 119.
- (4) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*, 2nd ed.; Kluwer: New York, 1999; p 52.
- (5) Tran, K.; Hanning-Lee, M. A.; Biswas, A.; Stiegman, A. E.; Scott, G. W. *J. Am. Chem. Soc.* **1995**, *117*, 2618.
- (6) (a) Curran, M. D.; Gedris, T. E.; Stiegman, A. E. *Chem. Mater.* **1999**, *11*, 1120. (b) Rice, G. L.; Scott, S. L. *J. Mol. Catal.* **1997**, *125*, 73.
- (7) Ruckschloss, M.; Wirschem, Th.; Tamura, H.; Ruhl, G.; Oswald, J.; Veprek, S. *J. Lumin.* **1995**, *63*, 279.
- (8) Soult, A. S.; Poore, D. D.; Mayo, E. I.; Stiegman, A. E. *J. Phys. Chem. B* **2001**, *105*, 2687.
- (9) Soult, A. S.; Carter, D. F.; Schreiber, H. D.; van de Burgt, L. S.; Stiegman, A. E. *J. Phys. Chem. B* **2002**, *106*, 9266.