

# Reply to the Comment on “Photoluminescence Study of the Introduction of V in Si-MCM-41: Role of Surface Defects and Their Associated SiO<sup>−</sup> and SiOH Groups”

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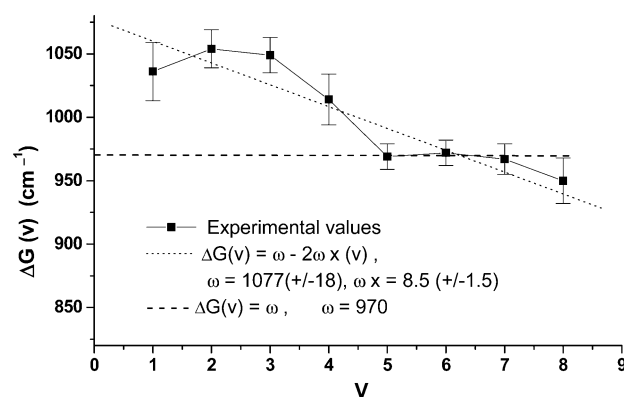
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We have read Stiegman's comment<sup>1</sup> on our paper.<sup>2</sup> His main points of contention concern (1) the assignment of the vibrational transition of the C<sub>3v</sub> pseudotetrahedral V species present in V-substituted mesoporous sieves (V-MCM-41) to the terminal V=O stretch and (2) the assignment of the emission bands at 420–620 nm to surface defects associated with SiO<sup>−</sup> and/or SiOH groups.

Concerning the first point, the argument developed in the comment is based primarily on the assertion that the vibronic structure observed in the photoluminescence induced around 19 000 cm<sup>−1</sup> in the vanadium-doped material cannot be attributed to a species involving a fundamental vibration around 1040 cm<sup>−1</sup> or more. A revised analysis is proposed by Stiegman who concludes that the spectral data are better reproduced using a vibronic progression involving a mode with a fundamental frequency around 970 cm<sup>−1</sup>, which must allegedly be reassigned to another species. To back up this claim, two spectral simulations are presented in Figures 1b,c<sup>1</sup> to illustrate unsatisfactory and satisfactory choices of parameters, respectively. These simulations, based on harmonic potentials for excited and ground states, involve in fact two distinct procedures: one is the reproduction of the *relative intensities* of the vibronic progression, using analytical formula developed for one-dimensional harmonic oscillator system, the second is the reproduction of the *frequencies* of the individual transitions, also based on the harmonic approximation and thus involving only two parameters *E*<sub>00</sub>, the electronic energy of the transition, and *ω*, the harmonic frequency of the chromophore in its ground state. These two points will now be addressed separately.

The relative intensities of the progression are the results of Franck–Condon factor calculations supposing harmonic potentials equal in the ground and excited states (no difference is mentioned), which is highly unlikely. Also, Stiegman assumes quite different and arbitrary reduced masses for the corresponding oscillators (*μ* = 16 (O) in Figure 1b, *μ* = 67 (O + V) in Figure 1c).<sup>1</sup> These choices are rather puzzling because they imply in the first case an oxygen atom and in the second a V=O group as a point mass, each vibrating against an infinite mass (which cannot be a Si atom of mass 28). The expression involved for a polyatomic fragment is more complicated and



**Figure 1.** Plot of energy spacing  $\Delta G(v)$  between vibronic components versus vibrational quantum number  $v$  for photoemission from vanadium sites in Si-MCM-41 from ref 2. The dotted line represents a least-squares fit linear regression with an anharmonic model, with  $\omega = 1077$  cm<sup>−1</sup> and  $\omega x = 8.5$  cm<sup>−1</sup>. The dashed line represents the result derived from Stiegman's analysis with  $\omega = 970$  cm<sup>−1</sup> ignoring anharmonicity.

will depend on the form of the normal coordinate involved. This casts doubt on the physical meaning of the internuclear coordinate change *S* in the calculation proposed. In sharp contrast to Stiegman's statement, even values near 0.13 Å are not unrealistic by comparison with precise data obtained on transition metal oxides.<sup>3,4</sup> In the case of CoO for which excitations in the same energy range (up to 21 000 cm<sup>−1</sup>) have been rotationally analyzed, the bond length is shown to increase by about 0.15 Å.<sup>3</sup> For VO precise data exist for excitations up to 19 000 cm<sup>−1</sup> only, but bond length variations reach 0.094 Å.<sup>4</sup>

A closer look at the differences between spectral simulations in Figure 1b,c<sup>1</sup> reveals that the most striking one does not concern relative intensities, but rather frequencies, i.e., the poor match between the stick positions and the experimental curve maxima in Figure 1b,<sup>1</sup> which brings us to the second, more important point. The frequencies (positions of the superimposed sticks in Figure 1b<sup>1</sup>) are supposed to be reproduced by a two-parameter (*E*<sub>00</sub> and *ω*) harmonic oscillator model. This is here simply inadequate, because anharmonicity plays a significant role on vibrational excitations observed in our case up to the ninth vibrational quantum number.<sup>2</sup> We will now expand the analysis, kept short in our paper,<sup>2</sup> because it had been published earlier for the V/SiO<sub>2</sub> system.<sup>5</sup>

Starting from the well-known expression for the vibrational energy:<sup>6</sup>

$$G(v) = \omega(v + 1/2) - \omega x(v + 1/2)^2 \quad (1)$$

where *ω* and *ωx* are the harmonic frequency and first-order anharmonic correction for the ground electronic state, respectively, and *v* is the vibrational quantum number. It is well-known that the energy spacing between two successive vibronic components will take the form

$$\Delta G(v) = G(v) - G(v - 1) = \omega - 2\omega x(v) \quad (2)$$

Such a plot using our experimental data is presented in Figure 1. Taking into account the experimental uncertainties on the frequencies and on a statistical treatment, a least-squares fit linear regression will yield best estimates for the harmonic frequency and anharmonicity of the mode involved in the

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vibronic progression,  $\omega = 1077 \pm 18 \text{ cm}^{-1}$  and  $\omega x = 8.5 \pm 1.5 \text{ cm}^{-1}$ , respectively. Input of these data into eq 2 for  $\nu = 1$  will lead to the best estimate for the fundamental vibration  $\Delta G(1) = 1060 \pm 21 \text{ cm}^{-1}$ , which can be compared with IR or Raman data. This value is compatible with the 1035–1070  $\text{cm}^{-1}$  range reported in the literature for surface V=O bonds,<sup>7–11</sup> not with Stiegman's value of 970  $\text{cm}^{-1}$ . Let us note finally that the energy spacings derived from the most intense peaks of the progression (0–5 to 0–7) are  $\Delta G(6) = 975 \pm 21 \text{ cm}^{-1}$  and  $\Delta G(7) = 958 \pm 21 \text{ cm}^{-1}$  in apparent good agreement with the spacing proposed by Stiegman in his oversimplified model (represented by the dashed line on Figure 1), but they do not reflect realistic values for the fundamental vibrational transition, important here for species identification.

Because of the controversy in the assignment of these transitions, Kawashima et al.<sup>12</sup> recently tried to clarify the nature of photoluminescence spectra of silica containing various concentrations of vanadium species. They found a vibrational frequency of about 1050  $\text{cm}^{-1}$  assigned to a terminal V=O stretching mode. Moreover, these authors pointed out that due to the anharmonicity of the potential it is not appropriate to use the averaged frequencies of the higher transitions modes, as Stiegman did.

Concerning the second point of Stiegman's comment, i.e., the photoluminescence observed at around 400–490 nm, we note that it has been reported for siliceous MCM-41 powder<sup>13</sup> and for our Si-MCM-41 and V-MCM-41 samples.<sup>2</sup> It is also interesting to note that the calcined siliceous MCM-41 does not exhibit strong photoluminescence in the wavelength region from 380 to 600 nm, whereas the laser irradiation at 250 nm leads to the dramatic enhancement of the photoluminescence at around 420 and 470 nm. These bands are attributed to oxygen-related defect sites such as peroxy radicals,  $E'$  centers, or nonbridging oxygen hole centers (NBOHC) on silica, and their formation is prevalent in silica with high OH content.<sup>13</sup> For our V-MCM-41 samples, the intensities of these bands decrease with increasing V content. A similar phenomenon has been previously observed upon introduction of vanadium ions into defects sites of dealuminated Si $\beta$ .<sup>14,15</sup> Along these arguments, it can be concluded that vanadium is incorporated at defect sites related to surface OH groups.

We do not think that the emission bands at 420–640 nm are related to impurities such as Sn or Ge, because the emission spectrum is quite different from that presented by Stiegman for 0.1 mol % Sn in silica (Figure 2).<sup>1</sup> In our opinion, the emission spectrum of the Si-MCM-41 sample (Figure 1b, ref 2) is very similar to that observed for OH-related centers in silica (Figure 2a, ref 16). In fact, in both cases three very broad emission bands appear at around 420, 470, and 600–640 nm.

All these features (absence, presence, or dependence of this photoluminescence on several factors) do not seem to be

explained solely in terms of Sn/Ge impurities, as suggested by Stiegman. They appear to be better explained in terms of and originate from SiO<sup>−</sup>/SiOH defect sites.

In conclusion, what remains from Stiegman's definitive comments?<sup>1</sup>

Concerning the analysis of the vibrational fine structure, the harmonic approximation used by Stiegman is too simple and *the neglect of anharmonicity*, already pointed out by previous authors,<sup>12</sup> can lead, as shown by Figure 1, *to serious error in the determination of the vibrational energy*.

Concerning the assignment of the photoluminescence at around 470 nm to Sn/Ge impurities, it seems also too simple to explain experimental results obtained by a number of authors on a wide range of samples, treated in various conditions, with vanadium species introduced by various methods either in crystalline or amorphous materials, and either in the bulk or on the surface of the material investigated. It nevertheless suggests that more attention be given to the content of Sn/Ge impurities in the samples, in particular to determine their contribution to the photoluminescence at 400–490 nm.

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## References and Notes

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