# Nitrogen substitutional defects in Silicon. A quantum mechanical characterization through the vibrational spectroscopy

Alexander Platonenko,[1] Fabien Pascale,[2] Francesco Silvio Gentile,[3] Anna Ferrari,[3] Maddalena D'Amore,[3] and Roberto Dovesi[3]

[1] *Institute of Solid State Physics, University of Latvia, 8 Kengaraga street, LV1063, Riga, Latvia*
[2] *Université de Lorraine – Nancy, CNRS, Laboratoire de Physique et Chimie Théoriques, UMR 7019. Vandœuvre-lès-Nancy, 54506 France*
[3] *Dipartimento di Chimica, Università di Torino and NIS (Nanostructured Interfaces and Surfaces) Centre, Via P. Giuria 5, 10125 Torino, Italy*

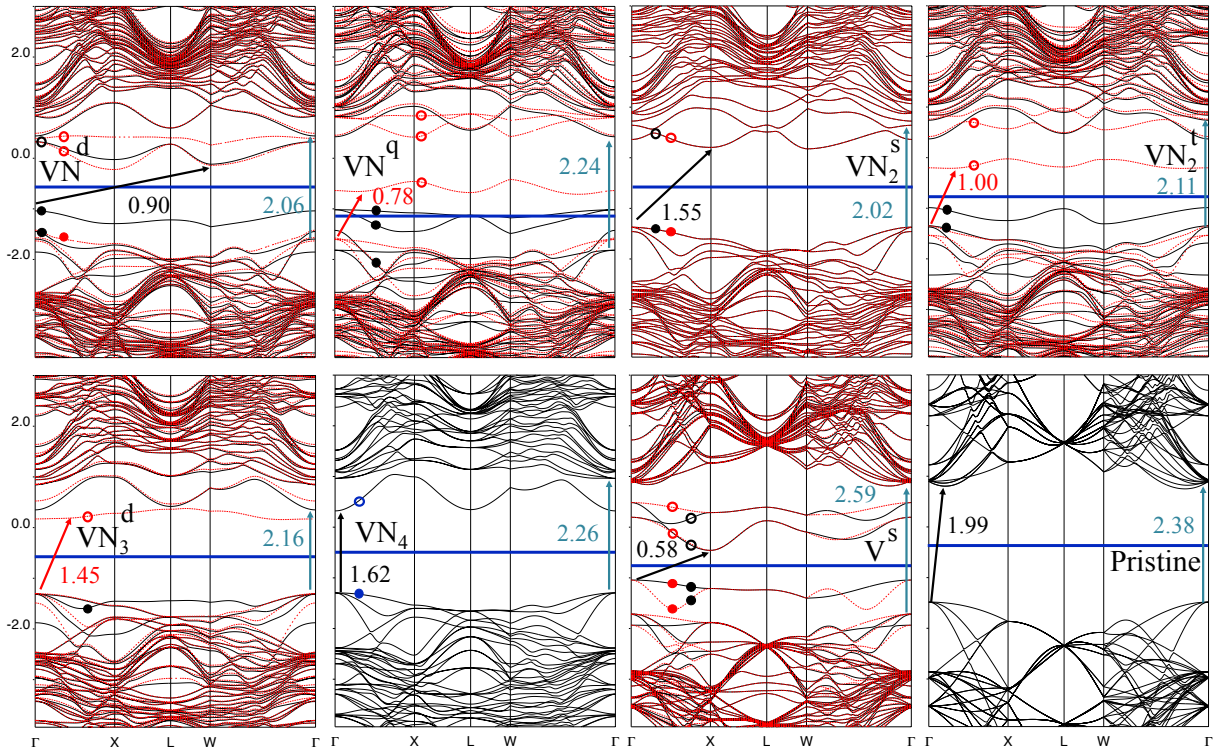


Figure S1: Band structure of the $VN_x$ defects in silicon compared with the silicon vacancy ($V^s$) and perfect silicon band structures. The $S_{64}$ supercell has been used and the lowest energy spin states have been taken into account. Superscripts q, t, d, s stand for quadruplet, triplet, doublet and singlet. The smallest band gap between $\alpha$ and $\beta$ defect levels have been indicated with black and red arrows respctively. Closed shell systems in blue. The black ($\alpha$) and red ($\beta$) circles represent the occupied (full circle) and unoccopied (empty circle) defect levels in the gap. The band gap of the perturbed hosting silicon structure (the difference between the top of the valence and the bottom of the virtual bands) is indicated by turquoise arrows.

In this document we present the band structure of many of the defects investigated in the main text, and the IR spectra of the high spin (and energy) states, when more than one spin state is possible.
For the $VN_1$ defect (top left panel of figure S1), the quadruplet state has three spin up electrons that occupy three defect bands (two of them are degenerate) in the band gap, just 0.4 eV above the top of the valence band. The gap for the spin-flip transition (alpha to beta) is around 0.3 eV. This would result in a doublet state. In the doublet band structure (second from the left top panel) gaps are much larger.
For the $VN_2$ defect, there are two bands (nearly degenerate) occupied by the two uncoupled electrons at about 0.3 eV above the top of the valence band. Here the gap for the spin-flip transition (alpha to beta) is around 0.7 eV. Such transition not only reduces the total energy of the system, but also shifts the defect bands from the gap to the valence bands region (see the $VN_2^s$ panel). The $VN_3$ unoccupied level lies very close to the bottom of the conduction band and the singly occupied defect level is very close to the valence band region. In the $VN_4^s$ case all bands are doubly occupied and fall down in the valence band region. For comparison, also the band structure of pristine silicon (bottom right) and of the defective vacancy, in the lowest energy singlet state, are reported.
In the $V_2N_2$ cases (see Figure S2) there are 4 uncoupled electrons, and then three possible spin states, namely a quintuplet Q, a triplet t and a singlet s. For the quintuplet state the gap between occupied alpha and unoccupied beta levels is barely visible, so

transition to triplet state would happen essentially at no cost. In the triplet (three up electrons, and then three $\alpha$ occupied bands, and one $\beta$ occupied band) gaps are larger, a trend that continues in the singlet state (two spin up and two spin down electrons).

The IR spectrum of the $VN^q$ case (figure S3, top), is very similar to the one of the lower energy solution: the spectrum is dominated by a single doubly degenerate peak at 654 $cm^{-1}$, that is associated with the N-$Si_3$ bonds in-plane stretching. In the $VN_2^t$ IR spectrum there are three active modes of $A_1$, $B_1$ and $B_2$ symmetry; their wavenumbers are however so close that they merge in a single peak. Also these modes are defect modes, involving the N-$Si_3$ atoms. The modes of the high-spin state are red-shifted when compared to the lower energy state.

The high spin (quintuplet) $V_2N_2$ (see Figure S4, top) spectrum is very similar to the $VN_2$ high-spin spectra. There are four active modes with high intensity that merge in a single peak. This peak is red shifted by about 10 $cm^{-1}$ with respect to the dominant peak of the low-spin spectrum. The triplet spectrum is extremely similar to the singlet one, for the reasons explained in the main text.

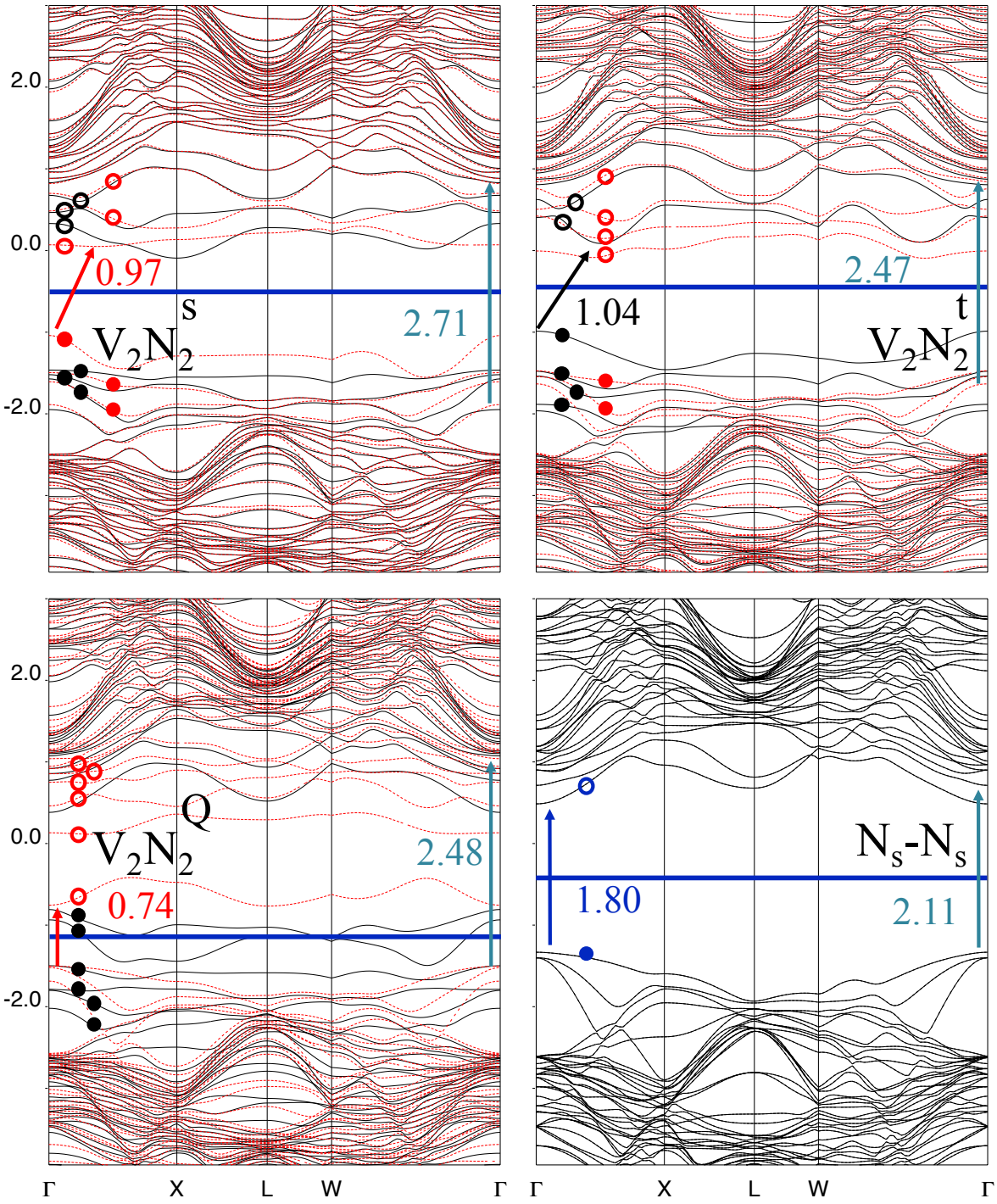


Figure S2: Band structure of the $V_2N_2$ defects in silicon. The $S_{64}$ supercell has been used and superscripts s, t, and Q stand for singlet, triplet and quintuplet. The smallest band gaps bteween $\alpha$ and $\beta$ defect levels have been indicated with black and red arrows respctively. The black ($\alpha$) and red ($\beta$) circles represent the occupied (full circle) and unoccopied (empty circle) defects in the gap. The blue color is adopted for closed shell systems. The band gap of the hosting Silicon structure (top of valence and bottom of virtual bands) is indicated by turquoise arrows.

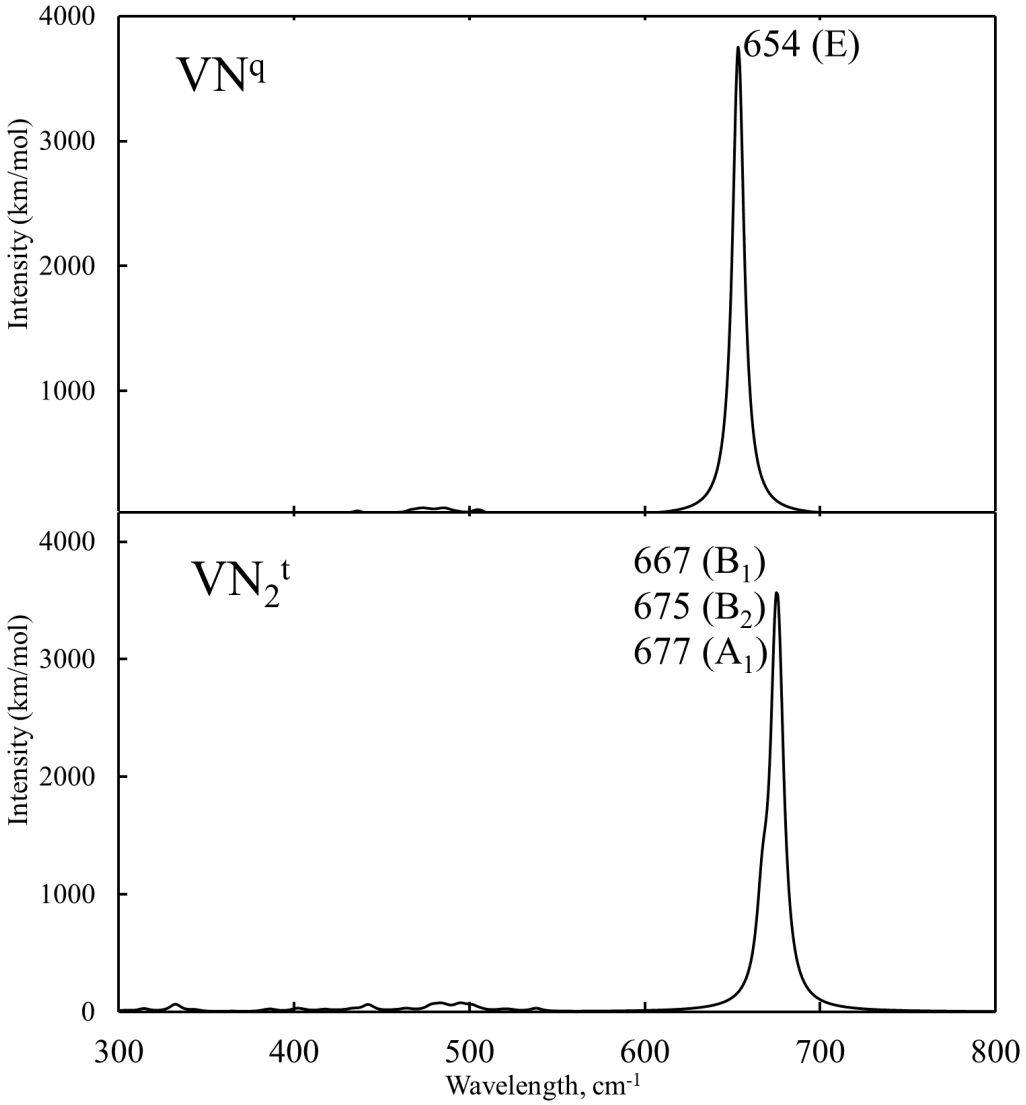


Figure S3: Simulated IR spectra of $VN_x$ defects in high spin and energy states. Superscripts q and t stand for quadruplet and triplet. In both cases the $S_{64}$ supercell has been used.

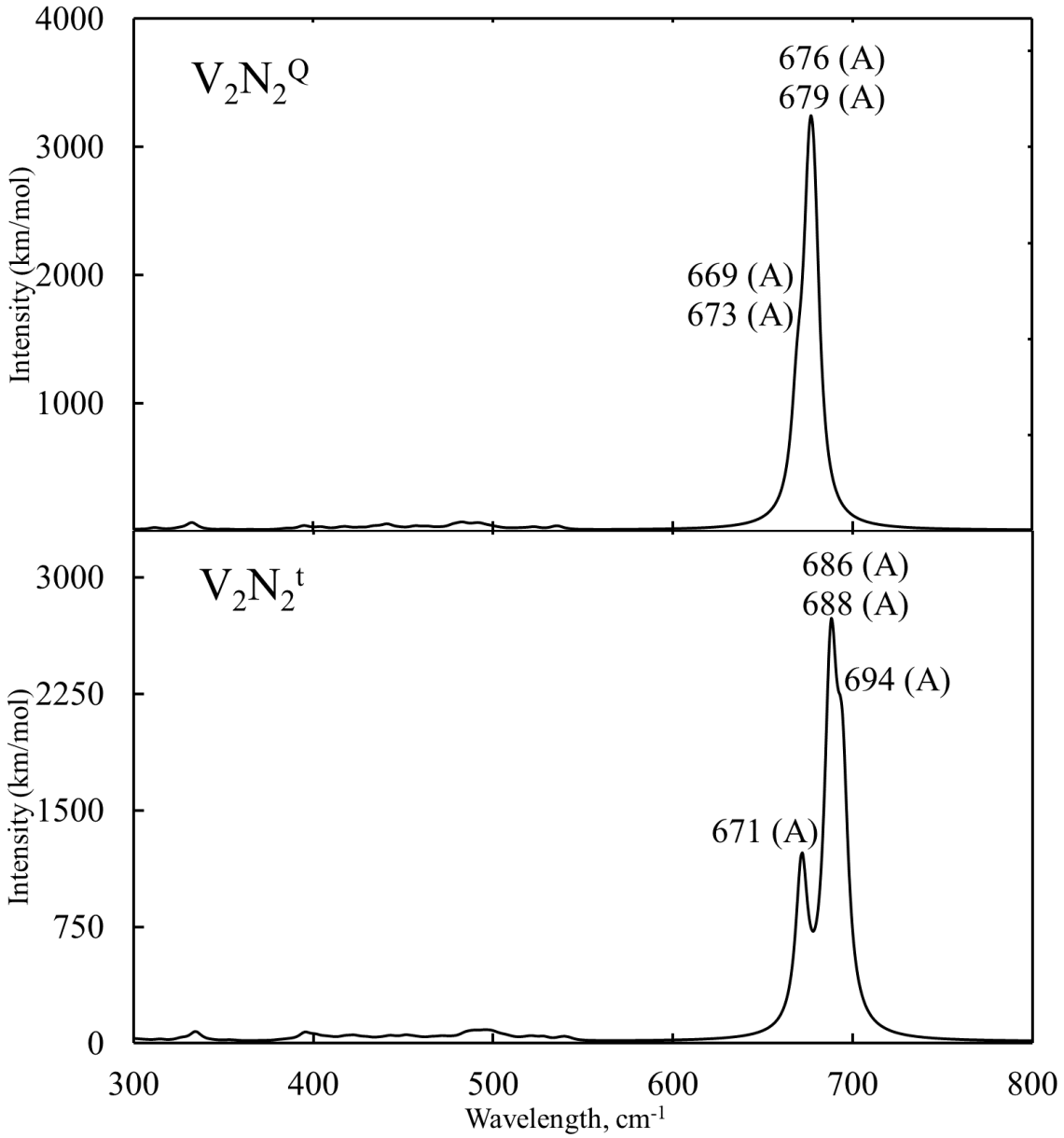


Figure S4: Simulated IR spectra of $V_2N_2$ defects in high spin and energy states. Superscripts Q and t stand for quintuplet and triplet. In both cases the $S_{64}$ supercell has been used.