

THEORETICAL MODELLING OF NUCLEAR RESONANCE VIBRATIONAL SPECTRA OF COMPLEX MOLECULES

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Abstract: The vibrational spectrum of an $\text{Fe}(\text{SH})_4^{-1}$ complex was calculated by Density functional Theory (DFT) frequency calculation and are optimized using the BP86 or B3LYP functionals and TZVP basis. Using a DFT approach, the normal mode composition factors and vibrational frequencies have been determined, and the nuclear resonance vibrational spectroscopy (NRVS) spectra have been fitted and simulated. The strong correlation between the experimental and calculated spectra allows for a clear interpretation of the NRVS data. These data provide important spectroscopic markers for high-valent Fe species and demonstrate the utility of this technique for the determination of Fe dynamics.

Key words: Nuclear resonance vibrational spectroscopy; DFT; BP86; B3LYP; Spectral simulation

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1. Introduction:

Nuclear resonance vibrational spectroscopy (NRVS) is a newly developed vibrational technique which utilizes synchrotron radiation generated at brilliant 3rd generation synchrotron radiation facilities like the Advanced Photon Source at Argonne National Lab. NRVS is closely related to Mossbauer spectroscopy, in which certain isotopes are constrained in solids to allow recoilless resonant absorption of incident gamma rays by the nucleus. Thus, the hyperfine structure of the probe nuclei can be observed. The probe nuclei vibrate along the molecular potential surface with vibrational energies on the order of tens of MeV. The nucleus can resonantly absorb photons with excess energy (ΔE) relative to the transition energy (E_0) of the probe nuclei, if E happens to create one vibrational quantum. If the energy is scanned over a reasonably large range, for example, -30~100 MeV around E_0 , a phonon spectrum of the probe nuclei can be obtained. NRVS is a valuable methodology recently applied in bioinorganic chemistry [1- 4]. For example, NRVS has been used to assign metal-ligand vibrational modes of diatomic molecules coordinated to porphyrins [4, 5, 6] and to detect nitrosylated iron-sulfur clusters in proteins [7, 8]. NRVS and density functional theoretical (DFT) studies of mononuclear Fe(III)-OOH [10 32] and Fe(IV)=O [9,10] compounds have provided insight into their distinctive chemical properties.

2. Computational methods:

The NRVS intensity derives exclusively from ^{57}Fe nuclei and directly depends on the vibrational frequencies and normal mode composition factors that characterize the extent of involvement of the resonant nucleus in a given normal mode [11, 12] The normal mode composition factors of ^{57}Fe (denoted as $e_{\text{Fe}\alpha}^2$, where index α refers to a normal mode) are determined by the molecular force fields, and thus their values reflect the details of the electronic structure.

In order to put the fitting on as sound as possible physical ground, we have carried out DFT frequency calculations performed at the BP86/TZVP level of theory. The DFT calculations provide the number of vibrational modes in the investigated frequency range, as well as initial guesses for the normal mode composition factors $e_{\text{Fe}\alpha}^2$ and vibrational frequencies. In order to avoid ambiguities and to minimize the number of free parameters, all line widths (FWHM, full width at half-height) were kept identical. After initial trials, the line shape was determined to be better represented by Lorentzians than by Gaussians, with a FWHM of 15.1 cm^{-1} .

All calculations were performed with the ORCA package [13, 14]. The structures of the models and experimental geometries of complexes were optimized using the BP86 or B3LYP functionals and TZVP basis [15]. In the geometry calculations, an intermediate grid for the electron density was used together with tight SCF convergence criteria. Figure 1 shows our calculated NRVS plot which we compare with the theoretical IR spectrum on the same scale. NRVS reports the Doppler broadening of the Moessbauer signal due to resonant scattering of phonons (vibrations) dominated by the Fe nuclei movements. This is a valuable addition to IR spectra where the corresponding vibrations might have very small intensity.

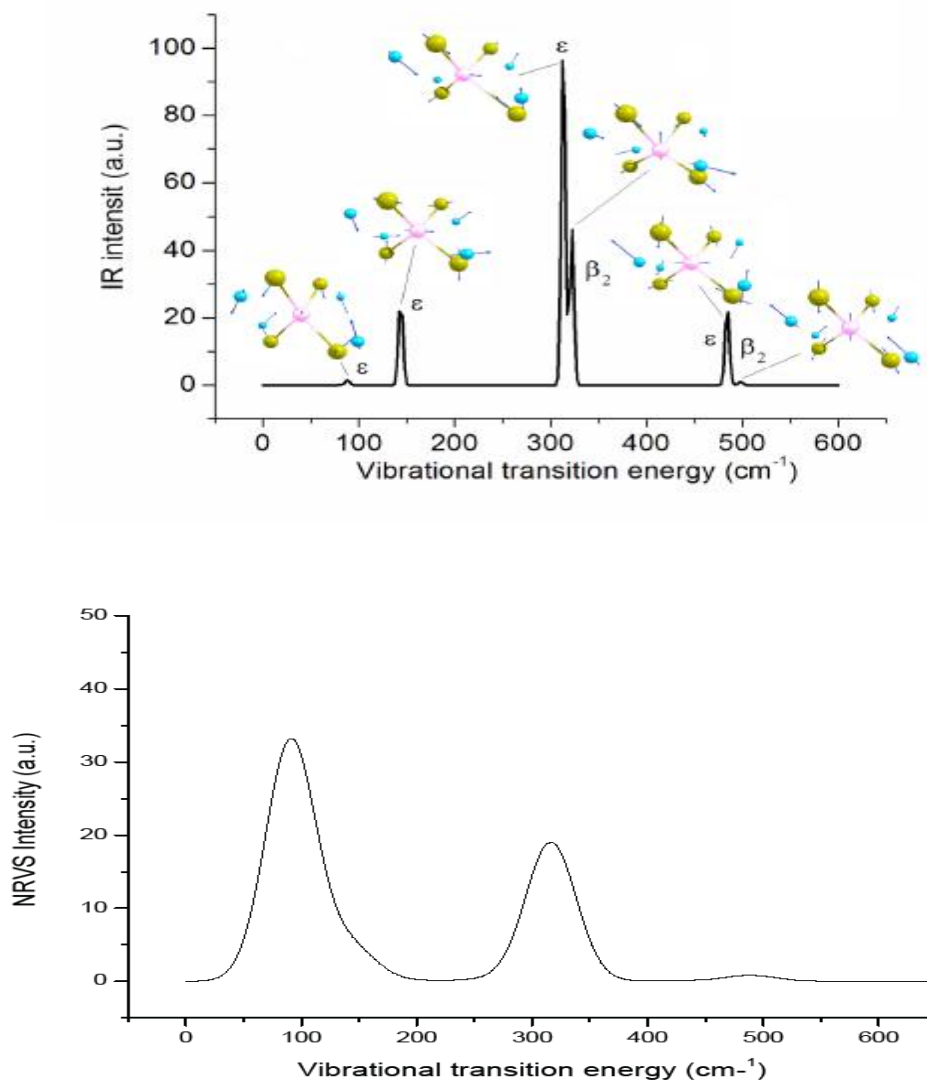
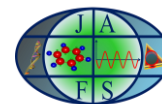


Figure 1: Theoretical IR spectrum with the shapes of vibrations dominating the IR intensity and NRVS scattering.

3. Conclusions and Discussion:

In this paper, we have summarized the details of our implementation of the NRVS into a quantum chemical code (ORCA). Normal mode composition factors provide a convenient means for the quantitative description of NRVS data. They can be calculated on the basis of the entire set of atomic displacements in a given normal mode [16-18]. In our approach, normal mode composition factors are determined in an equivalent but more compact form as appropriate components of an orthogonal matrix that diagonalizes the Hessian matrix.



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