Dear Colleges,

The first version of the local mode program LModeA is available. LModeA can be applied with minimal computational costs after a harmonic vibrational frequency calculation, optionally using measured frequencies as additional input, leading to a wealth of information on molecular structure and bonding. In addition a comprehensive analysis of IR/Raman spectra can be performed. Interfaces to the most common quantum chemical packages are available. Our vision is that both experimental and computational spectroscopists will routinely apply LModeA in the future, enriching our chemical knowledge.



Figure 1: Flowchart of the local mode program LModeA

As shown in Figure 1, LModeA takes input information from a vibrational frequency calculation including (1) Cartesian coordinates, (2) Hessian matrix, (3) atomic masses and (4) atomic polar tensors for intensities (if applicable). It contains interfaces for the most commonly used quantum chemistry packages, ensuring that LModeA is generally available and does not depend on the use of a particular quantum chemical software. Important to note is that experimental frequencies can also be used for the analysis. The local mode parameters to be used can be defined in terms of internal coordinates including bond lengths, bond angles, and dihedral angles, but LModeA also supports the use of curvilinear coordinates for local mode studies of intermediates during dynamic processes such as ring inversion, ring pseudo rotation, and bond pseudo rotation in Jahn-Teller systems¹⁻⁴ and Cremer-Pople ring puckering and deformation coordinates⁵ recently applied to the study of the interplay of ring puckering and hydrogen bonding in deoxyribonucleosides.⁶ Other parameters include out-of-plane angles, pyramidalization angles, or parameters defined with regard

to *dummy atoms* as needed for the description of strong and weak metal– π interactions. LModeA will then produce local mode data and if requested perform a characterization of normal mode analysis. Python scripts interface the LModeA output data to graphics software.

Please contact **Dr. Marek Freindorf (mfreindorf@smu.edu) or Dr. Elfi Kraka (ekraka@smu.edu)** to receive a copy of the source code, installation instructions, manual and tutorial.

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Short description of the local mode theory:

For a comprehensive description see: E. Kraka, W. Zou, and Y. Tao. "Decoding chemical information from vibrational spectroscopy data: Local vibrational mode theory". WIREs: Comput. Mol. Sci., page e1480, 2020.

With the increasing number of available high precision measured and calculated spectra, vibrational spectroscopy could become an excellent source for decoding the electronic structure of a molecule and for providing a new quantitative measure of the intrinsic strength of a chemical bond. However, normal vibrational modes in a molecule are always coupled, therefore they cannot be used as a direct measure of bond strength.^{7–9} As a suitable measure of the intrinsic bond strength, local mode force constants were derived from the local vibrational mode theory originally developed by Konkoli and Cremer.^{10–14} There are two coupling mechanisms between the vibrational modes, *electronic coupling* associated with the potential energy content of a vibrational mode and *mass coupling* associated with the kinetic energy content. The electronic coupling between the normal vibrational modes is caused by the off-diagonal elements of the force constant matrix **F** and can be eliminated by diagonalizing **F**, i.e. solving the fundamental equation of vibrational spectroscopy,¹⁵

$$\mathbf{F}^{\mathbf{q}} \mathbf{D} = \mathbf{G}^{-1} \mathbf{D} \mathbf{\Lambda} \tag{1}$$

where $\mathbf{F}^{\mathbf{q}}$ is the force constant matrix in internal coordinates \mathbf{q} and \mathbf{G} is the Wilson mass-matrix. Matrix \mathbf{D} collects the normal mode eigenvectors \mathbf{d}_{μ} and the diagonal matrix $\mathbf{\Lambda}$ collects the vibrational eigenvalues $\lambda_{\mu} = 4\pi^2 c^2 \omega_{\mu}$, where ω_{μ} represents the harmonic vibrational frequency of mode \mathbf{d}_{μ} given in reciprocal cm, c is the speed of light, and $\mu = (1 \cdots N - L; N:$ number of atoms in the molecule, L = 5 for linear and 6 for non-linear molecules). Solution of Eq.1 leads to the diagonal force constant \mathbf{K} given in normal coordinates \mathbf{Q} which is free of electronic coupling:

$$\mathbf{K}^{\mathbf{Q}} = \mathbf{D}^{\dagger} + \mathbf{F}^{\mathbf{q}} \mathbf{D}$$
 (2)

However, mass coupling is still present when the electronic coupling is eliminated by solving the Wilson equation, a fact which has frequently been overlocked. Konkoli and Cremer¹⁰ determined for the first time local, mass-decoupled vibrational modes a_i directly from normal vibrational modes d_{μ} by solving the mass-decoupled Euler-Lagrange equations. The subscript *i* specifies an internal coordinate q_i and the local mode is expressed in terms of normal coordinates Q associated with force constant matrix K^Q of Eq.2. The local vibrational modes are unique and they can be based on either calculated or experimentally determined vibrational frequencies.

$$\mathbf{a}_{i} = \frac{\mathbf{K}^{-1}\mathbf{d}_{i}^{\dagger}}{\mathbf{d}_{i} \mathbf{K}^{-1} \mathbf{d}_{i}^{\dagger}}$$
(3)

To each local mode \mathbf{a}_i , a corresponding local mode frequency ω_i^a , local mode mass $G_{i,i}^a$, and a local force constant k_i^a can be defined.¹⁰ The local mode frequencies can be uniquely connected to the normal mode

frequencies via an adiabatic connection scheme.¹⁶ The local mode frequency ω_i^a is defined by:

$$(\omega_i^a)^2 = \frac{G_{i,i}^a k_i^a}{4\pi^2 c^2}$$
(4)

and the force constant k_i^a by:

$$k_i^a = \mathbf{a}_i^\dagger \mathbf{K} \mathbf{a}_i \tag{5}$$

Local mode force constants, contrary to normal mode force constants, have the advantage of being independent of the choice of the coordinates used to describe the molecule in question and in contrast to local vibrational frequencies they are independent of the atomic masses. They are extremely sensitive to differences in the electronic structure (e.g., caused by changing a substituent) and they capture only electronic effects. As shown by Zou and Cremer¹⁷ local mode stretching force constants can be directly associated with the intrinsic strength of a chemical bond and/or weak chemical interaction.



Figure 2: Overview of local mode applications regarding bonding and weak chemical interactions

Based on this landmark paper local vibrational stretching force constants force have been successfully applied to assess the strength of strong and weak covalent bonds, ^{17–24} to investigate weak chemical interactions including hydrogen, halogen, pnicogen, chalcogen and tetrel bonding, ^{6,6,19,25–31,31–44} to derive a new description of meta-ligand bonding, ^{32,35,45–49} and a new aromaticity index, ^{16,47,50,51} as depicted in Figure 2.

There exists a 1:1 relationship between a complete set of non-redundant local modes and the normal modes via an *adiabatic connection scheme*, allowing a smooth transition from local to normal modes.¹⁶ This forms the basis of the characterization of normal mode (CNM) procedure.¹³ CNM decomposes each normal mode into local mode contributions offering a new, comprehensive way of analyzing IR and Raman spectra, which we successfully applied to assess the usefulness of vibrational Stark effect probes,⁵² as shown for a popular CN probe in Figure 3. Recently, the local mode theory was extended for the description of chemical bonding in periodic systems and crystals.^{53,54}



Figure 3: Normal mode decomposition into local modes for a popular Start effect probe

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