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Research paper

The normal modes of vibration of benzene from the trajectories of stress tensor eigenvector projection space

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ABSTRACT

A QTAIM and Stress tensor eigenvector projection U_σ space formalism has been used to provide a detailed description of the participation of each of the bonds of the four infrared active normal modes of benzene. Analysis of the maximum U_σ space trajectory projections revealed a mixture of C—C and C—H bonding characteristics. The four infrared active U_σ space trajectories were found to be unique. The normal mode with the highest infrared intensity was the only mode with non-zero maximum U_σ space trajectory projections in the most preferred and least preferred directions for the C—C and C—H bond critical points respectively.

A great deal of theoretical work has been carried out on the normal coordinate treatment of benzene [1–3]. Wilson [2] in particular, suggested a simplified potential function with six force constants. Manneback obtained the most general potential function compatible with the simple harmonic approximation and with the D_{6h} symmetry of benzene [4].

Experimental and theoretical investigations of the vibration modes of benzene have become increasingly complete due to refined laboratory techniques and increased computational power. The vibrational modes of benzene have been extensively studied using semiempirical and *ab initio* methods [5–7]. We will focus on the infrared (IR) active normal modes of vibration [2,8–10] because the IR Intensity (10^{-7} cm^2 mol^{-1} s^{-1} ln) are non-zero unlike the Raman modes, see Table S1 of Supplementary Materials S1. Therefore we can use QTAIM and the stress tensor to explain the relative differences in the intensities of the IR active modes. Infrared (IR) active modes have associated changes in the dipole moment [8–12] with larger dipole moment leading to greater intensity of the normal mode of vibration, see Scheme 1 and the accompanying caption.

The conventional treatment assigns particular modes as comprising particular bond types C—C, C—H or mixed but is unable to quantify how the bonds move or how they are distorted, either by being stretched, compressed or bent. Therefore, it is not possible to accurately determine the extent to which particular bonds participate in a given normal mode of vibration. The goal of this work is therefore to create a new methodology to quantify both the distortion and movement of the bonds and in so doing gain new insights into the subtle details of the normal modes of benzene. This will be undertaken without the need for expensive atomic integrations so the method is applicable to any molecule. We will use the quantum theory of atoms in molecules (QTAIM) [13] and the stress tensor trajectories T_σ in the stress tensor eigenvector projection space U_σ [14,15]. QTAIM will be used to quantify the bond distortion, that is, stretching, contraction and bending of the bonds. The stress tensor trajectories T_σ will be used to relate the change in position of each of the bond critical points (*BCPs*) and a given frame of reference, which is described in terms of the eigenvectors of the Hessian of the total charge density distribution $\rho(\mathbf{r})$ of the equilibrium benzene structure. In this investigation we will use Bader's definition of the stress tensor [16,17].

Using QTAIM we are concerned with the chemical properties obtained from analyzing the properties of the Hessian matrix of the charge density $\rho(\mathbf{r})$ evaluated at each critical point. A diagonalization of the Hessian matrix of $\rho(\mathbf{r})$ gives the set of ordered eigenvalues $\lambda_1 < \lambda_2 < \lambda_3$, with the Laplacian $\nabla^2\rho(\mathbf{r})$ of the electron density $\rho(\mathbf{r})$ being the algebraic sum of these eigenvalues evaluated at one of the four types of critical point which are connected by the Poincaré–Hopf relation: $n - b + r - c = 1$.

These four types of critical point, n, b, r, and c, are given by the numbers of nuclear critical point (*NCPs*), bond critical points (*BCPs*), ring critical points (*RCPs*), and cage critical points (*CCPs*), respectively. The description in real space of the nature of the topology of the total electronic charge density distribution $\rho(\mathbf{r})$ is condensed into the *molecular graph* [18–20], which is defined as the set of critical points and associated bond-paths.

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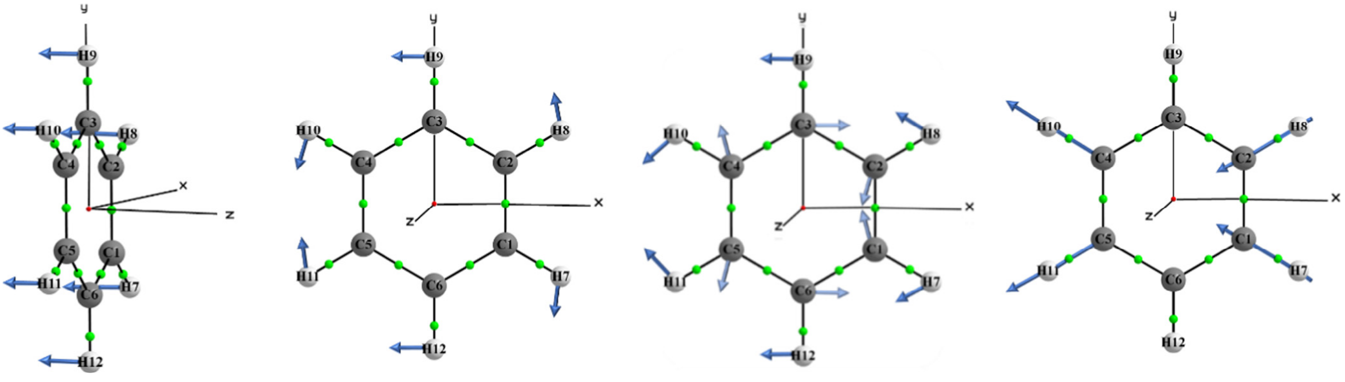

benzene_0005 benzene_0014 benzene_0021 benzene_0028

Scheme 1. The conventional rendering of four normal modes of benzene are superimposed onto the molecular graphs of the relaxed structure of benzene. The four infrared (IR) active normal modes of benzene are ordered according to their increasing frequency, corresponding to 721.568 cm^{-1}, 1097.691 cm^{-1}, 1573.927 cm^{-1} and 3298.320 cm^{-1} respectively, the arrows are not drawn to scale, see Supplementary Materials S1 for the complete list of the frequencies, intensities and experiment activity for all $3N - 6 = 30$ normal modes of vibration. The corresponding intensities (10^{-7} cm^2 mol^{-1} s^{-1} ln) are 136.47, 5.78, 10.92 and 24.86 respectively.

A diagonalization of the Hessian matrix of $\rho(\mathbf{r})$ also gives the set of ordered eigenvectors $\underline{\mathbf{e}}_1$, $\underline{\mathbf{e}}_2$, $\underline{\mathbf{e}}_3$, where the eigenvector $\underline{\mathbf{e}}_3$ indicates the direction of the bond-path at the *BCP*. In QTAIM the most and least preferred directions of electron accumulation are $\underline{\mathbf{e}}_{\mathbf{2}}$ and $\underline{\mathbf{e}}_{\mathbf{1}}$, respectively [21–23], for the stress tensor the most and least preferred direction of motion of electrons and *BCP*s are indicated by the $\underline{\mathbf{e}}_{\mathbf{1\sigma}}$ and $\underline{\mathbf{e}}_{\mathbf{2\sigma}}$ eigenvector respectively. Motion along the bond-path is indicated by $\underline{\mathbf{e}}_{\mathbf{3\sigma}}$.

The stress tensor eigenvector based descriptors can be used to track the changing orientation of the stress tensor ($\underline{\mathbf{e}}_{\mathbf{1\sigma}}$, $\underline{\mathbf{e}}_{\mathbf{2\sigma}}$, $\underline{\mathbf{e}}_{\mathbf{3\sigma}}$) eigenvectors of the benzene *BCP*s with respect to the passage of the normal mode of vibration. The eigenvector projections will be performed for each of the ($\underline{\mathbf{e}}_{\mathbf{1\sigma}}$, $\underline{\mathbf{e}}_{\mathbf{2\sigma}}$, $\underline{\mathbf{e}}_{\mathbf{3\sigma}}$) in two directions; the positive and negative displacements from the equilibrium state. The stress tensor eigenvector trajectories $\mathrm{T}_{\sigma}(s)$ are constructed from the set of shifts $\mathbf{dr}(s)$, associated with steps s, of a given *BCP* in 3-D Cartesian space as an ordered set of vectors $\mathbf{dr}$ ▫ (s) in the stress tensor eigenvector projection space U_{σ}, where $\mathbf{dr}$ ▫ $(s) = \{\mathbf{dr}(s).\underline{\mathbf{e}}_{\mathbf{1\sigma}}, \mathbf{dr}(s).\underline{\mathbf{e}}_{\mathbf{2\sigma}}, \mathbf{dr}(s).\underline{\mathbf{e}}_{\mathbf{3\sigma}}\}$. In this investigation, the order of shifts $\mathbf{dr}(s)$ used to generate the trajectory $\mathrm{T}_{\sigma}(s)$ is associated with following the normal mode of vibration pathway from the equilibrium state to the appropriate maximum displacement in the amplitude. Additionally, for a given *BCP*, the stress tensor eigenvectors,$\{\underline{\mathbf{e}}^{\mathbf{ES}}_{\mathbf{1\sigma}}, \underline{\mathbf{e}}^{\mathbf{ES}}_{\mathbf{2\sigma}}, \underline{\mathbf{e}}^{\mathbf{ES}}_{\mathbf{3\sigma}}\}$ for that *BCP* in the equilibrium state are used as the projection set for the entire trajectory $\mathrm{T}_{\sigma}(s)$, where the superscript '**ES**' refers to equilibrium state.

In this work we examine four of the thirty normal modes of benzene. These are chosen since they are the infrared (IR) active modes. The hyphenated numbers (e.g. benzene_0005) used to label the benzene normal modes refer to the mode number, see Supplementary Materials S1.

The geometry optimization and frequency calculation were carried out using the BHandHLYP DFT functional and 6-31G(d,p) basis set in G09 v.E.01 [24]. The SCF convergence criteria were set to tighter values than the defaults, specifically to both $<10^{-10}$ RMS change in the density matrix and $<10^{-8}$ maximum change in the density matrix. Single-point calculations, corresponding to snapshots throughout one full cycle of each of the calculated vibrational modes, were carried out using the same functional, basis set and convergence criteria. The intermediate 'snapshot' structures were generated by an external program using the geometry-optimized structure together with the displacement directions calculated for each mode in the frequency calculation. The wavefunctions produced by the snapshot single-point calculation were then analyzed using AIMAll [25] and the resulting molecular graphs analyzed using two in-house codes, the first to calculate the eigenvector projections and the second to filter, visualize and measure the resulting U_{σ} space trajectories, see Supplementary Materials S5.

The molecular graphs of the four IR active modes corresponding to the maximum positive and negative displacements are given in Fig. 1. The complete set of thirty benzene normal modes including the experiment activity assignments are provided in Supplementary materials S1. The excess BPL (bond-path length) incurred during normal modes are presented in Table 1. The real space lengths (l) in a.u. of the Trajectory pathways for the infrared active normal modes of benzene are provided in Supplementary materials S2 and the stress tensor projection space U_{σ} pathways L_{σ} are provided in Supplementary Materials S3**.** The variation of the stress tensor eigenvalue $\lambda_{3\sigma}$ with displacement is provided in Supplementary materials S4**.** The trajectory pathways in the stress tensor projection space U_{σ} are presented in Fig. 2. The procedure to generate the trajectory length L_{σ} in the stress tensor eigenvector projection space U_{σ} and smooth trajectory pathways is provided in Supplementary materials S5. The maximum projections $\{(\underline{\mathbf{e}}_{\mathbf{1\sigma}}\ \mathbf{dr})_{\max}, (\underline{\mathbf{e}}_{\mathbf{2\sigma}}\ \mathbf{dr})_{\max}, (\underline{\mathbf{e}}_{\mathbf{3\sigma}}\ \mathbf{dr})_{\max}\}$ in the stress tensor eigenvector projection space U_{σ} are presented in Table 2.

The details of the structural distortion of the benzene molecule as a consequence of undergoing the infrared (IR) active normal mode oscillations are apparent from the molecular graphs shown for the maximum positive and maximum negative displacements in Fig. 1. The consequences of these normal modes on the benzene structure are not as apparent in the conventional treatment in Scheme 1.

Firstly, we use QTAIM to quantify the details of the structural distortion by comparing the excess bond-path length (BPL) at the maximum positive displacement, equivalent to the maximum negative displacement, compared with the BPL of the equilibrium geometry benzene, see Table 1. This treatment takes into consideration both the stretching, or contraction, of the bond-paths as well as the bending of the bond-paths, e.g. the C3—C9 *BCP* and C6—H12 *BCP* bond-paths in Fig. 1(c) due to the action of the normal mode of vibration. The clear differentiation between the excess BPL distortions of the C—C *BCP* and C—H *BCP* in benzene_0005, the IR active mode with the greatest intensity is seen from Table 1, see also Supplementary Materials S1 and Scheme 1. The conventional treatment of the benzene_0014 and benzene_0028 normal modes