



Study of Energy Flow using *Ab-Initio* Molecular Dynamics: Application to OH Radical Adducts in Gas Phase and Adsorbed on an Aerosol.



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Abstract

Investigation of Intramolecular Vibrational Energy Redistribution can provide insights into the reactivity of molecules of interest. Recently, we presented a method to gain insight into the mechanism of energy flow between the different vibrational modes of the OH radical adducts of isoprene and butadiene. The mechanism of energy flow was investigated by analyzing the time evolution of the dynamical spectra obtained using *ab initio* molecular dynamics. Furthermore, the harmonic mode-couplings are also analyzed as part of this formalism to unravel the energy flow [1, 2]. As an extension, we studied the effect of adsorption onto an atmospheric aerosol, modeled by the isoprene-OH adduct and a water cluster. In both of these studies the vibrational spectra retrieved from molecular dynamics was analyzed by decomposing the spectrum into the contributions from each of a set of normal vibrational modes. Although the same technique will be used in both systems, two complementary styles of application will illuminate different vibrational properties during the dynamics.

Introduction

- Intramolecular Vibrational Energy Redistribution (IVR) has long been considered to be an important factor in stabilizing a reaction intermediate.
- Recently [1], experimental studies on the pressure dependent rate constants of butadiene and isoprene with OH radicals have shown that the butadiene-OH reaction is pressure independent while isoprene-OH was pressure dependent above room temperature for pressures between 1-6 Torr.
- The reasons for this difference in observed pressure dependence could be attributed to
 - Difference in stability of the OH radical adducts for the reaction of butadiene and isoprene with OH radical,
 - Difference in pathways available for dissipation of energy in the OH radical adducts, i.e. the rate of Intramolecular Vibrational Energy Redistribution.
- To investigate the mechanism of energy flow, we use the Dynamical Normal Mode Decomposition recently introduced by our group to study the decomposition of finite temperature AIMD spectra [3].
- Interaction with atmospheric aerosol droplets can also have important implications on the energy flow of such systems. Dramatic changes in rate constants, stereo- and regioselectivity have been observed in reactions occurring on the surface of water [4]. This effect is due to the enhanced hydrogen bonding available at the liquid/gas interface.
- As a model for the shared proton stretch between an adsorbate and an aerosol, a second set of calculations were performed for isoprene-OH on a water cluster. Dynamical Normal Mode Decomposition was used as a tool in analyzing the properties of the shared proton stretch.

Dynamical Normal Mode Decomposition

- We expand the Fourier transform of the mass weighted velocity vectors for MD simulation time t' in a basis of the normal modes derived from the Hessian matrix which form a complete set of vectors as

$$\vec{V}^{t'}(\omega) = \sum_i C_i^{t'}(\omega) * \vec{H}_i$$

where $C_i^{t'}(\omega) = \vec{H}_i \cdot \vec{V}^{t'}(\omega)$.

- The net contribution from normal mode, i , in the frequency range $\Delta\omega = [\omega_1, \omega_2]$ may be written as

$$C_{i,t'}^{\Delta\omega} = \left[\int_{\omega_1}^{\omega_2} d\omega \left| \vec{H}_i \cdot \vec{V}^{t'}(\omega) \right|^2 \right]^{1/2}$$

- The predominance of vibrational modes in a region of the spectrum can be estimated from the projection of the Fourier Transform of the Velocity Auto-Correlation (FT-VAC) onto the normal modes.
 - This same idea has been used in our group to understand the differences between infrared multiple-photon dissociation and argon tagged vibrational action spectroscopy in proton bound ether systems. [3]
- The t' -dependent evolution of the critical harmonic components over a range of frequencies of interest provides insight into the mechanisms and couplings of vibrational energy transfer.
- Conversely, the ω -dependent contribution throughout the vibrational spectrum made by a specified normal mode can also be determined; case in point being the shared proton stretch of the isoprene-OH/water cluster.

Results and Discussion

OH radical adducts in Gas Phase

- We have carried out *ab-initio* Molecular Dynamics (AIMD) simulations to investigate the mechanism of energy flow in the OH radical adducts [1, 2].
- The adduct molecule was divided into three fragments for distribution of kinetic energies, and the flow of energy from the fragment with highest kinetic energy to that with the lowest kinetic energy was observed.
- For each of the adduct molecules, simulations were carried out for an initial configuration with an asymmetric distribution of kinetic energies. The third fragment always has less kinetic energy compared to fragments I and II.
- The spectra associated with this energy flow was analyzed using the FT-VAC at intervals of 2ps.
- The FT-VAC was decomposed using the Dynamical Normal Mode Decomposition for various ranges of frequency to analyze the dominant modes involved in energy flow in that frequency range.

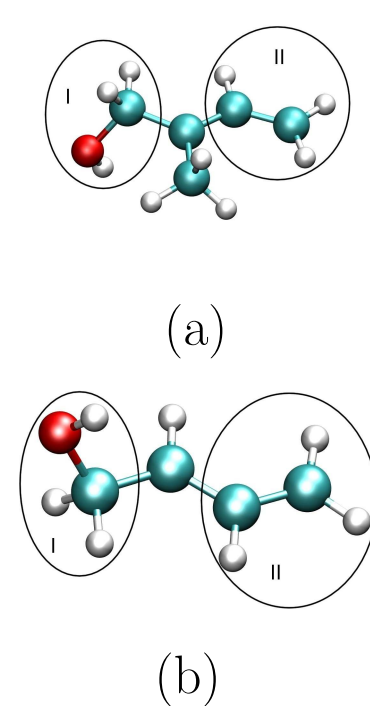


FIGURE 1: Structure of (a) isoprene and (b) butadiene OH adducts showing the three fragments for AIMD simulations.

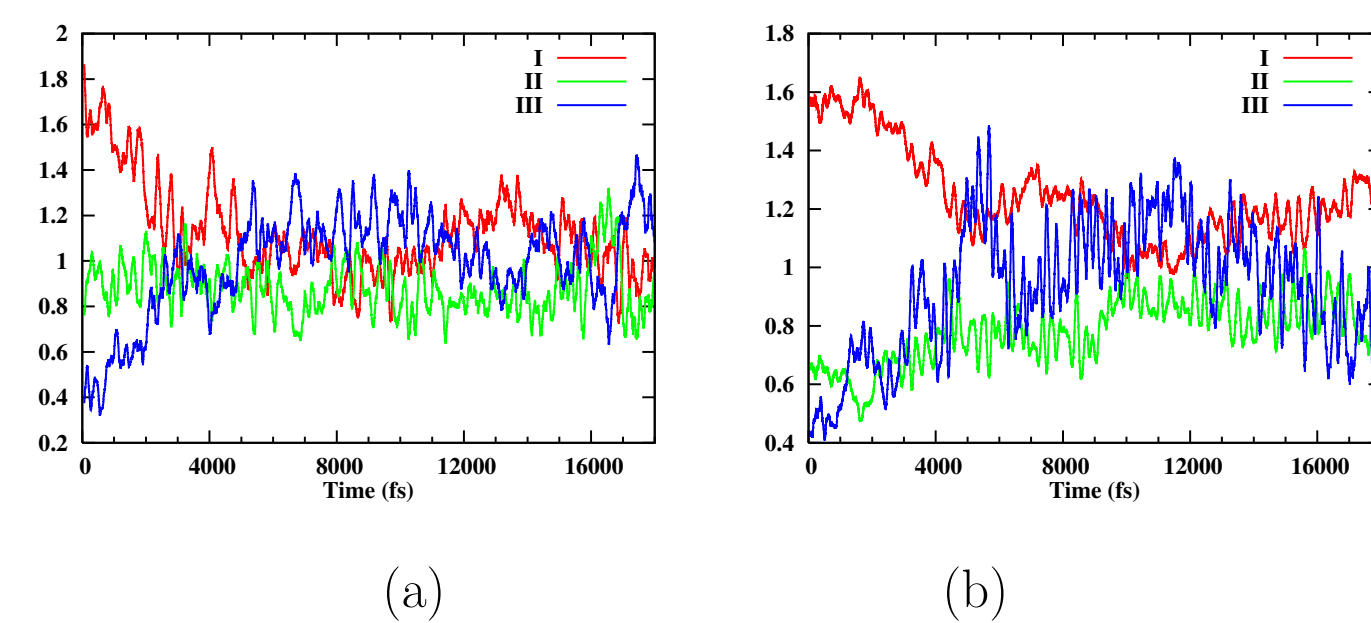


FIGURE 2: Time evolution of the kinetic energy quotients (see text) of the three fragments for adduct 1 of (a) isoprene-OH and (b) butadiene-OH for an initial configuration with kinetic energy of fragment I greater than that of fragment II.

- In Figs. 3 and 4, we provide the time evolution of the harmonic components for the OH radical adducts in the frequency range $\Delta\omega = [1200 - 1800] \text{ cm}^{-1}$, computed from the FT-VAC at every 2ps intervals. These results provide evidence for the exchange of energy between the most dominant harmonic modes in this frequency range.

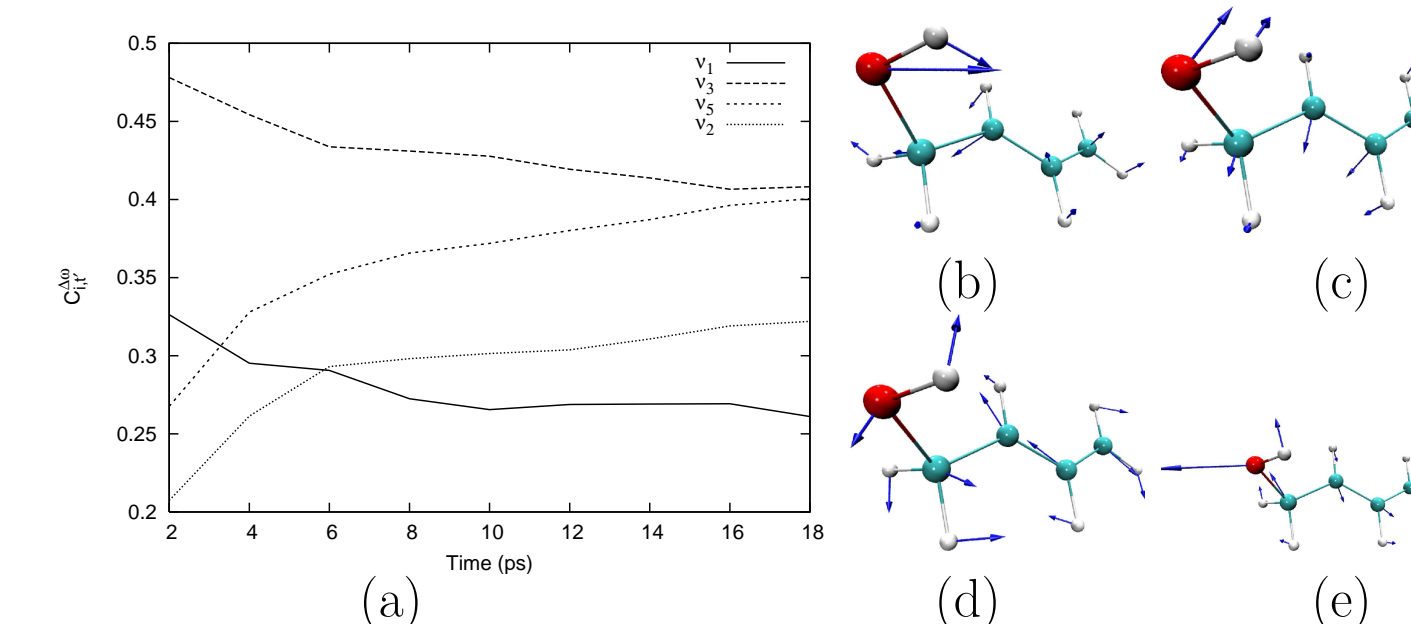


FIGURE 3: The t' -dependent evolution of the harmonic components, $C_{i,t'}^{\Delta\omega}$, of the butadiene-OH adduct 1 in the frequency range $\Delta\omega = [1200 - 1800] \text{ cm}^{-1}$. Harmonic modes (b) ν_1 , (c) ν_2 , (d) ν_3 and (e) ν_5 correspond to the four dominant modes. The modes ν_1 and ν_2 represent torsional motions about the C1-C2 single bond that exchange energy, while ν_3 and ν_5 represent orthogonal wags of the entire network about the C1-C2 bond.

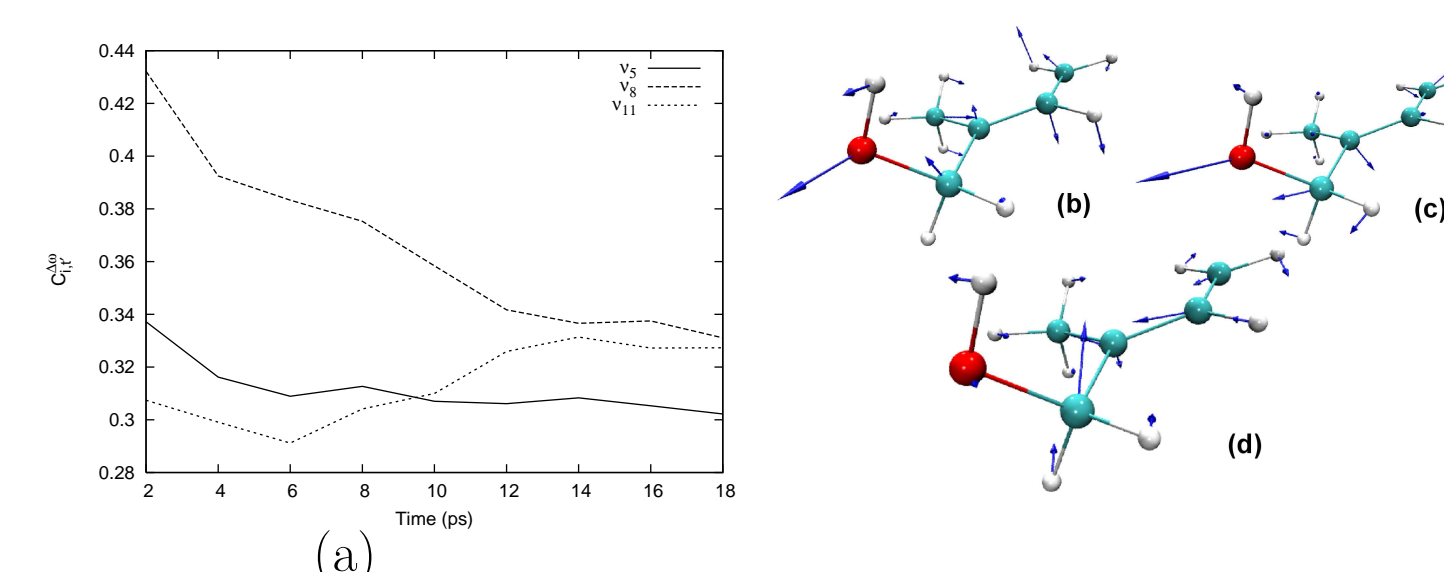


FIGURE 4: The t' -dependent evolution of the harmonic components, $C_{i,t'}^{\Delta\omega}$, of the isoprene-OH adduct 1 in the frequency range $\Delta\omega = [1200 - 1800] \text{ cm}^{-1}$. Harmonic modes (b) ν_5 , (c) ν_8 and (d) ν_{11} correspond to the dominant modes. The plots indicate an energy exchange from ν_5 , ν_8 to ν_{11} all of involve the open-jaw motion of the five-membered O-C-C-C-H ring.

Isoprene-OH radical adsorbed on an Aerosol

- Optimizations and frequency calculations were performed with various numbers of water molecules using B3LYP/6-31G(d) in order to determine effects of cluster size on properties of the shared proton stretch and the system in general.

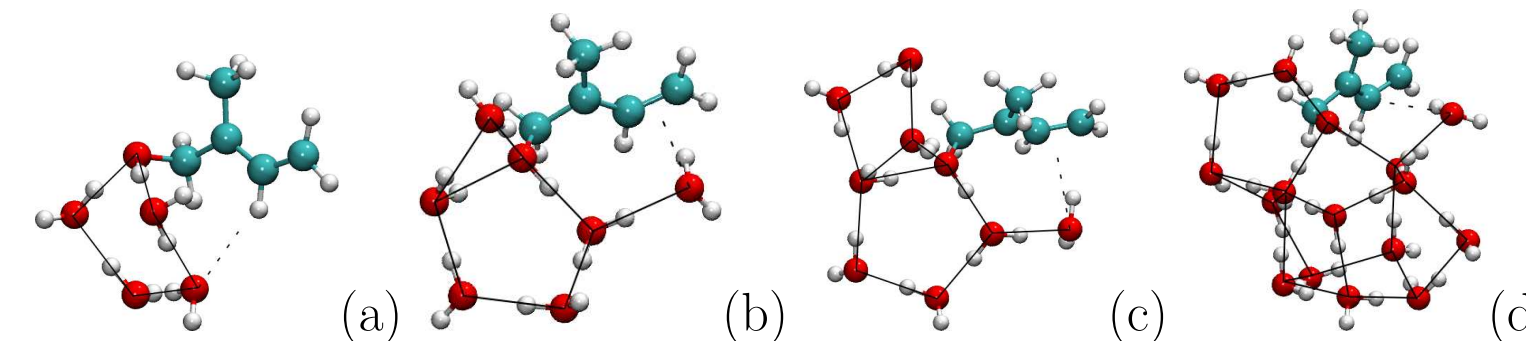


FIGURE 5: Isoprene-OH adduct with 4 (a), 6 (b), 8 (c) and 15 waters (d).

- Two trends identified as functions of cluster size include an increase in adsorbate/cluster binding energy and red shift of the shared proton stretch, both of which peaked around six to eight waters.

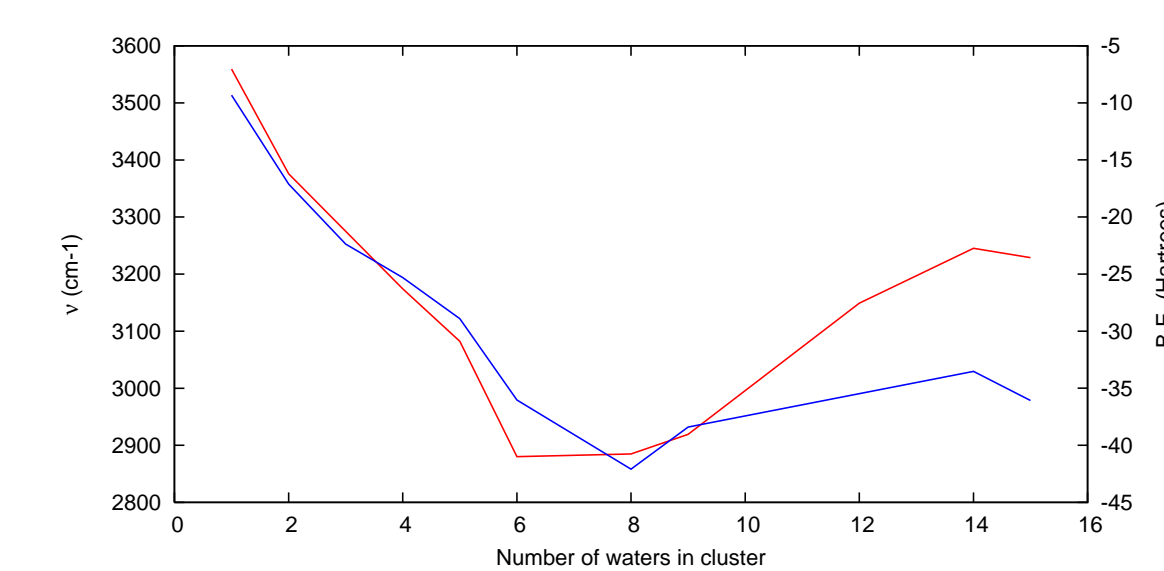


FIGURE 6: Isoprene-OH/water cluster binding energy (blue) and shared proton stretch harmonic frequency (red) as functions of cluster size defined by the number of waters.

- AIMD of the six and eight water clusters yielded a velocity spectrum which entirely lacked a peak for the shared proton stretch which had been prominent in the harmonic frequency calculations.
- A normal mode decomposition of the FT-VAC velocity spectrum showed a large delocalized frequency range over which the shared proton stretch contributed intensity. This spreading out of the stretching frequency is a significant dynamic averaging effect captured in the dynamic vibrational spectrum.
- This dynamical averaging is very much reminiscent of that seen in other hydrogen bonded systems studied in our group, eg. $H^+(H_2O)_{21}$, $OH^-(H_2O)_6$, $Me_2O..H..OMe_2^+$, $Me_2O..D..OMe_2^+$ [3, 5].

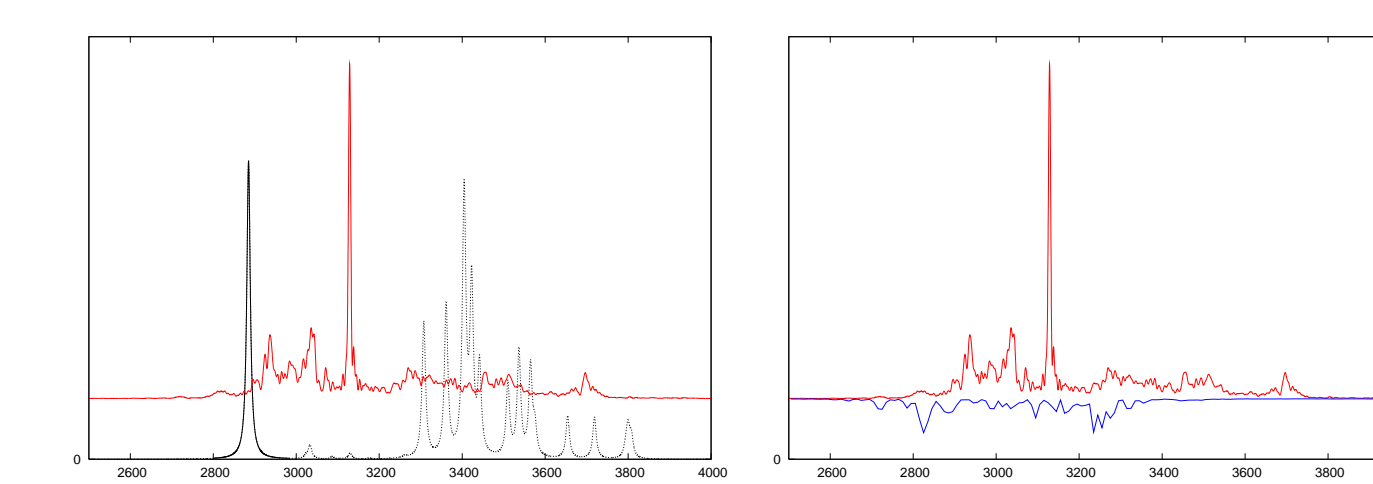


FIGURE 7: Vibrational spectra of isoprene-OH on the eight water cluster from 2500 to 4000 wavenumbers: FT-VAC vibrational spectrum (red), shared proton stretch harmonic normal mode contribution (blue) and the infrared harmonic frequency calculation (dashed). The shared proton stretch peak is made solid in the harmonic IR spectrum.

Conclusions

- The Dynamical Normal Mode Decomposition presented here is a useful tool for decomposing vibrational spectra into components along harmonic normal modes and give a better understanding of intra- and intermolecular energy flow among various vibrational modes.
- Our results on the OH radical adducts of isoprene and butadiene provide evidence for a difference in the mechanism for the dissipation energy in the two adducts resulting in difference in the rate of IVR.
- More specifically, the vibration modes involving the five-membered ring in the gas phase isoprene-OH adduct are seen to participate in energy flow, stabilizing the adduct.
- The shared proton stretch in isoprene-OH adduct adsorbed on a water cluster exhibits significant broadening due to time averaging and anharmonicity. This along with its position suggests that will be one of the important mediators of intermolecular vibrational energy dissipation.
- In this work, we have presented a method to study vibrational energy flow in molecular systems. In addition, we have provided applications using two different analysis schemes:
 1. time evolution of the normal mode contributions to the total dynamical spectrum.
 2. frequency dependent contribution of a given normal mode to the intensity of the spectrum.

References

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