Naval Research Laboratory

Washington, DC 20375-5320

NRL/MR/6390--12-9392

Terahertz Spectra of Water Complexes of β-HMX Calculated by Density Functional Theory

L. Huang
S.G. Lambrakos
N. Bernstein
V. Jacobs

Center for Computational Materials Science
Materials Science and Technology Division

A. Shabaev

George Mason University
Fairfax, Virginia

L. Massa

Hunter College
New York, New York

March 16, 2012

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 16-03-2012	**2. REPORT TYPE** NRL Memorandum Report	**3. DATES COVERED** *(From - To)* October 1, 2011 – January 30, 2012

4. TITLE AND SUBTITLE

Terahertz Spectra of Water Complexes of β-HMX Calculated by Density Functional Theory

5a. CONTRACT NUMBER

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

L. Huang, S.G. Lambrakos, N. Bernstein, V. Jacobs, A. Shabaev,* and L. Massa†

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER
63-9874-B-2-5

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Naval Research Laboratory, Code 6394
4555 Overlook Avenue, SW
Washington, DC 20375-5320

8. PERFORMING ORGANIZATION REPORT NUMBER

NRL/MR/6390--12-9392

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
One Liberty Center
875 North Randolph Street, Suite 1425
Arlington, VA 22203-1995

10. SPONSOR / MONITOR'S ACRONYM(S)
ONR

11. SPONSOR / MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

*George Mason University, Department of Computation and Data Sciences, Fairfax, VA 22030
†Hunter College, City University of New York, New York, NY 10065

14. ABSTRACT

The need for better detection of explosive devices has imposed a necessity for determining the dielectric response properties of energetic materials with respect to electromagnetic wave excitation. Among the range of different frequencies for electromagnetic excitation, the THz frequency range is of particular interest because of its nondestructive nature. The present study is based on significant progress in density functional theory (DFT), and associated software technology, which is sufficiently mature for the determination of dielectric response functions, and actually provides complementary information to that obtained from experiment. This point is further demonstrated in this study by calculations of ground state resonance structure associated with water complexes of the high explosive β-HMX using density functional theory (DFT), which is for the construction of parameterized dielectric response functions for excitation by electromagnetic waves at frequencies within the THz range. These dielectric functions provide for different types of analyses concerning the dielectric response of explosives. In particular, these dielectric response functions provide quantitative initial estimates of spectral response features for subsequent adjustment with respect to additional information such as laboratory measurements and other types of theory based calculations. With respect to qualitative analysis, these spectra provide for the molecular level interpretation of response structure. The DFT software GAUSSIAN was used for the calculations of ground state resonance structure presented here.

15. SUBJECT TERMS

Density functional theory (DFT)
Dielectric functions
Ground state resonance
Water complexes

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON**
					Samuel G. Lambrakos
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**	UU	26	**19b. TELEPHONE NUMBER** *(include area code)*
Unclassified	Unclassified	Unclassified			(202) 767-2601

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39.18

Contents

Introduction

A quantitative understanding of the dielectric response properties of high explosives with respect to electromagnetic wave excitation was motivated in the past by the need for monitoring munitions stockpiles under control of the US Navy, as well as defense related organizations. This was necessary in that stored explosives are typically characterized by shelf lives and tend to degrade with time, as well as being subject to environmental influences associated with storage, which can contribute to either their degradation or instability. In addition to understanding the dielectric response of individual explosives, as pure systems, it was necessary to understand their dielectric response as a component of a layered composite material. This was necessary in that many explosives, as used in practice, are a composite of binding material, whose purpose can be both chemical and structural. It follows that, in the past, a primary motivation for quantitative understanding of dielectric properties of high explosives was for purposes of accessing energetic materials performance. The current need for better detection of explosive devices, however, has imposed a new motivation for quantitative understanding of dielectric response properties of high explosives with respect to electromagnetic wave excitation. This motivation is the goal of better detecting improvised explosive devices (IEDs), which is in contrast to the goal of better accessing the materials performance of industrially fabricated explosives for munitions purposes.

Among the range of different frequencies for electromagnetic excitation, for purposes of IED detection, the THz frequency range is of particular interest because of its nondestructive nature and ability to penetrate materials that are characteristic of clothing. Typically, the dielectric response properties for electromagnetic wave excitation at THz frequencies, as well as at other frequencies, are determined by means of experimental measurements. The present study is based on significant progress in density functional theory (DFT), and associated software technology, which is sufficiently mature for the determination of dielectric response functions, and actually provides complementary information to that obtained from experiment. In particular, these dielectric response functions provide quantitative initial estimates of spectral response features that can be adjusted with respect to additional information such as laboratory measurements and other types of theory based calculations, as well as providing for the molecular level interpretation of response structure.

Density functional theory has been successfully used to investigate the vibrational spectra of energetic materials in the form of single molecules and molecular crystals [1-7]. These calculations provide detection signatures for various forms of materials, which can be encountered in various detection scenarios [8,9]. The isolated-molecule simulation results help to identify intramolecular vibrational modes in the absorption spectra of various materials. A series of studies have focused on the general concept of constructing dielectric response functions using DFT for the purpose of quantitative simulation of explosives detection scenarios [9,10,11]. As emphasized in these studies, the construction of permittivity functions using DFT calculations, defines a general approach where dielectric response is estimated within the bounds of relatively well-defined adjustable parameters. Following this approach, permittivity functions are constructed using DFT calculated absorption spectra under the condition that the calculated resonance locations are fixed, while resonance widths and number densities are assumed adjustable with respect to additional information such as experimentally observed spectra.

Manuscript approved January 30, 2012.

Previous studies [9,10,11], of which this work is a continuation, considered the calculation of ground state resonance structure associated with single isolated molecules of various high explosives. With respect to practical application, these calculations are relevant for construction of dielectric response functions for detector designs where explosives tend to be in gas phase, distributed over a surface, or in general, distributed uniformly within some ambient environment as single molecules. In what follows, calculations are presented of ground state resonance structure associated with water complexes of the high explosive β-HMX. It is significant to note that, with respect to practical application, water complexes represent an important special case for constructing dielectric response functions using DFT calculations. This special case concerns single isolated molecules interacting with a water environment. With respect to practical applications, i.e., detector design, this special case is significant in that a wide range of explosives detection environments include water as a major component. Accordingly, the dielectric response functions to be adopted for detection within these environments are weighted averages of the dielectric responses of noninteracting water complexes of explosives and the ambient environment within which the water complexes are distributed.

A significant aspect of using response spectra calculated by density functional theory, DFT, for the direct construction of dielectric response functions is that it adopts the perspective of computational physics, according to which a numerical simulation represents another source of “experimental” data. This perspective is significant in that a general procedure may be developed for construction of dielectric response functions using DFT calculations as a quantitative initial estimate of spectral response features for subsequent adjustment with respect to additional information such as experimental measurements and other types of theory based calculations. That is to say, for the purpose of simulating many electromagnetic response characteristics of materials, DFT is sufficiently mature for the purpose of generating data complementing, as well as superseding, experimental measurements.

In the case of THz excitation of materials, the procedure of using response spectra calculated using DFT, which is associated with ground state resonance structure, for the direct construction of permittivity functions is well posed owing to the physical characteristic of THz excitation. In particular, it is important to note that the procedure for constructing a permittivity function using response spectra calculated using DFT is physically consistent with the characteristically linear response associated with THz excitation of molecules. Accordingly, one observes a correlation between the advantages of using THz excitation for detection of explosives (and ambient materials) and those for its numerical simulation based on DFT. THz excitation does not appreciably induce electronic transitions. Moreover, in the linear (low-intensity) regime, THz excitation can be treated by means of perturbation theory. Of course, the practical aspect of the perturbative character of THz excitation for detection is that detection methodologies can be developed which do not damage materials under examination. The perturbative character of THz excitation with respect to molecular states has significant implications with respect to its numerical simulation based on DFT. It follows then that, owing to the perturbative character of THz excitation, which is characteristically linear, one is able to make a direct association between local oscillations about ground-state minima of a given molecule and THz excitation spectra.

Construction of permittivity functions according to the best fit of available data for a given material corresponding to many different types of experimental measurements has been typically the dominant approach. This approach is extended by using DFT calculations of electromagnetic response as data for construction of permittivity functions. The inclusion of this type of information is significant for accessing what spectral response features at the molecular level are actually detectable with respect to a given set of detection parameters. Accordingly, permittivity functions having been constructed using DFT calculations provide a quantitative correlation between macroscopic material response and molecular structure. Within this context it is not important that the permittivity function be quantitatively accurate for the purpose of being adopted as input for system simulation. Rather, it is important that the permittivity function be qualitatively accurate in terms of specific dielectric response features for the purpose of sensitivity analysis, which is relevant for the assessment of absolute detectability of different types of molecular structure with respect to a given set of detection parameters. That is to say, permittivity functions that have been determined using DFT can provide a mechanistic interpretation of material response to electromagnetic excitation that could establish the applicability of a given detection methodology for detection of specific molecular characteristics. Within the context of practical application, permittivity functions having been constructed according to the best fit of available data would be “correlated” with those obtained using DFT for proper interpretation of permittivity-function features. Subsequent to establishment of good correlation between DFT and experiment, DFT calculations can be adopted as constraints for the purpose of constructing permittivity functions, whose features are consistent with molecular level response, for adjustment relative to specific sets of either experimental data or additional molecular level information.

The calculations presented here of ground state resonance structure associated with water complexes of the high explosive β-HMX are for the construction of parameterized dielectric response functions for excitation by electromagnetic waves at compatible frequencies. For this purpose the DFT software GAUSSIAN09 (G09) was adopted [12]. The organization of the subject areas presented here are as follows. First, a brief description of the elements of vibrational analysis using DFT relevant for the calculation of absorption spectra is presented. Second, a general review is presented concerning the formal structure of permittivity functions in terms of analytic function representations. An understanding of the formal structure of permittivity functions in terms of both physical consistency and causality is important for post-processing of DFT calculations for the purpose of constructing permittivity functions. Third, information concerning the ground state resonance structure of water complexes of the high explosive β-HMX, which is obtained using DFT, is presented. This information consists of the ground state molecular geometry and response spectrum for a single isolated molecule and water complexes of β-HMX. Fourth, a discussion is presented that elucidates the utility of information concerning the ground state resonance structure of water complexes of explosives. This discussion also suggests procedures for the construction of permittivity functions that are in terms of reduced sets of phenomenological parameters. Finally, a conclusion is given summarizing the significance of modeling the dielectric response of molecular clusters relative to explosives detection in practice.

Construction of Dielectric Response Functions using DFT

As in previous studies [9,10,11] the formal mathematical structure underlying DFT calculations, as well as the procedure for constructing permittivity functions using these calculations, is included here for purposes of completeness. A brief description of this mathematical structure is as follows.

The DFT software GAUSSIAN09 (G09) can be used to compute an approximation of the IR absorption spectrum of a molecule or molecules [12]. This program calculates vibrational frequencies by determining second derivatives of the energy with respect to the Cartesian nuclear coordinates, and then transforming to mass-weighted coordinates at a stationary point of the geometry [13]. The IR absorption spectrum is obtained using density functional theory to compute the ground state electronic structure in the Born-Oppenheimer approximation using Kohn-Sham density functional theory [14-18]. GAUSSIAN uses specified orbital basis functions to describe the electronic wavefunctions and density. For a given set of nuclear positions, the calculation directly gives the electronic charge density of the molecule, the potential energy V, and the displacements in Cartesian coordinates of each atom. The procedure for vibrational analysis followed in GAUSSIAN is that described in [19]. Reference [20] presents a fairly detailed review of this procedure. A brief description of this procedure is as follows.

The procedure followed by GAUSSIAN is based on the fact the vibrational spectrum depends on the Hessian matrix $\mathbf{f}_{\mathrm{CART},}$ which is constructed using the second partial derivatives of the potential energy V with respect to displacements of the atoms in Cartesian coordinates. Accordingly, the elements of the $3N$ x $3N$ matri*x* $\mathbf{f}_{\mathrm{CART}}$ are given by

$$f_{\mathrm{CART}ij} = \left(\frac{\partial^2 V}{\partial\xi_i \partial\xi_j}\right)_0 \tag{1}$$

where $\{\xi_1, \xi_2, \xi_3, \xi_4, \xi_5, \xi_6, ..., \xi_{3N}\} = \{\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, ..., \Delta z_N\}$, which are displacements in Cartesian coordinates, and N is the number of atoms. As discussed above, the zero subscript in Eq.(1) indicates that the derivatives are taken at the equilibrium positions of the atoms, and that the first derivatives are zero. Given the Hessian matrix defined by Eq.(1) the operations for calculation of the vibrational spectrum require that the Hessian matrix Eq.(1) be transformed to mass-weighted Cartesian coordinates according to the relation

$$f_{\mathrm{MWC}ij} = \frac{f_{\mathrm{CART}ij}}{\sqrt{m_i m_j}} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_0 \tag{2}$$

where $\{q_1, q_2, q_3, q_4, q_5, q_6, ..., q_{3N}\} = \left\{\sqrt{m_1}\Delta x_1, \sqrt{m_1}\Delta y_1, \sqrt{m_1}\Delta z_1, \sqrt{m_2}\Delta x_2, \sqrt{m_2}\Delta y_2, \sqrt{m_2}\Delta z_2, ..., \sqrt{m_N}\Delta z_N\right\}$ are the mass-weighted Cartesian coordinates. GAUSSIAN computes the energy second derivatives Eq.(2), thus computing the forces for displacement perturbations of each atom along each Cartesian direction. The first derivatives of the dipole moment with respect to atomic positions $\partial\vec{\mu}/\partial\xi_i$ are also computed. Each vibrational eigenmode leads to one peak in the absorption spectrum, at a frequency equal to the mode's eigenfrequency ν_{n0}. The absorption intensity corresponding to a particular eigenmode n whose eigenfrequency is ν_{n0} is given by

$$I_n = \frac{\pi}{3c}\left|\sum_{i=1}^{3N} \frac{\partial\vec{\mu}}{\partial\xi_i} l_{\mathrm{CART}in}\right|^2, \tag{3}$$

where $\mathbf{l}_{\mathrm{CART}}$ is the matrix whose elements are the displacements of the atoms in Cartesian coordinates. The matrix $\mathbf{l}_{\mathrm{CART}}$ is determined by the following procedure. First,

$$\mathbf{l}_{\mathrm{CART}} = \mathbf{M}\mathbf{l}_{\mathrm{MWC}}, \tag{4}$$

where $\mathbf{l}_{\mathrm{MWC}}$ is the matrix whose elements are the displacements of the atoms in mass-weighted Cartesian coordinates and $\mathbf{M}$ is a diagonal matrix defined by the elements

$$M_{ii} = \frac{1}{\sqrt{m_i}}. \tag{5}$$

Proceeding, $\mathbf{l}_{\mathrm{MWC}}$ is the matrix needed to diagonalize $\mathbf{f}_{\mathrm{MWC}}$ defined by Eq.(2) such that

$$(\mathbf{l}_{\mathrm{MWC}})^{\mathrm{T}} \mathbf{f}_{\mathrm{MWC}}(\mathbf{l}_{\mathrm{MWC}}) = \Lambda, \tag{6}$$

where Λ is the diagonal matrix with eigenvalues λ_i. The procedure for diagonalizing Eq.(6) consists of the operations

$$\mathbf{f}_{\mathrm{INT}} = (\mathbf{D})^{\mathrm{T}} \mathbf{f}_{\mathrm{MWC}}(\mathbf{D}) \tag{7}$$

and

$$(\mathbf{L})^{\mathrm{T}} \mathbf{f}_{\mathrm{MWC}}(\mathbf{L}) = \Lambda, \tag{8}$$

where $\mathbf{D}$ is a matrix transformation to coordinates where rotation and translation have been separated out and $\mathbf{L}$ is the transformation matrix composed of eigenvectors calculated according to Eq.(8). The eigenfrequencies in units of (cm^{-1}) are calculated using the eigenvalues λ_n by the expression

$$\nu_{n0} = \frac{\sqrt{\lambda_n}}{2\pi c} \ , \tag{9}$$

where c is the speed of light. The elements of $\mathbf{l}_{\mathrm{CART}}$ are given by

$$l_{\mathrm{CART}ki} = \sum_{j=1}^{3N} \frac{D_{kj} L_{ji}}{\sqrt{m_j}} \ , \tag{10}$$

where k, $i=1,\ldots, 3N$, and the column vectors of these elements are the normal modes in Cartesian coordinates.

The intensity Eq.(3) must then be multiplied by the number density of molecules to give an absorption-line intensity in the non-interacting molecule approximation. It follows that the absorption spectrum calculated by GAUSSIAN is a sum of delta-function components, whose line positions and coefficients correspond to the vibrational-transition frequencies and the absorption-line intensities, respectively. In principle, however, these spectral components must be broadened and shifted to account for anharmonic effects such as finite mode lifetimes and inter-mode couplings.

The construction of permittivity functions using DFT calculations requires that a specific parametric function representation be adopted. This parametric representation must be physically consistent with specific molecular response characteristics, while limiting the inclusion of feature characteristics that tend to mask response signatures that may be potentially detectable. In principle, parameterizations are of two classes. One class consists of parameterizations that are directly related to molecular response characteristics. This class of parameterizations would include spectral scaling and width coefficients. The other class consists of parameterizations that are purely phenomenological and are structured for optimal and convenient best fits to experimental measurements. A sufficiently general parameterization of permittivity functions is given by Drude-Lorentz approximation [21]

$$\varepsilon(\nu) = \varepsilon'(\nu) + i\varepsilon''(\nu) = \varepsilon_\infty + \sum_{n=1}^{N} \frac{\nu_{np}^2}{(\nu_{no}^2 - \nu^2) - i\gamma_n \nu} \ , \tag{11}$$

where ν_{np} and γ_n are the spectral scaling and width of a resonance contributing to the permittivity function. The permittivity ε_∞ is a constant since the dielectric response at high frequencies is substantially detuned from the probe frequency. The real and imaginary parts, $\varepsilon_r(\nu)$ and $\varepsilon_i(\nu)$, respectively, of the permittivity function can be written separately as

$$\varepsilon_r(\nu) = \varepsilon_\infty + \sum_{n=1}^{N} \frac{\nu_{np}^2(\nu_{no}^2 - \nu^2)}{(\nu_{no}^2 - \nu^2)^2 + \gamma_n^2 \nu^2} \quad \text{and} \quad \varepsilon_i(\nu) = \sum_{n=1}^{N} \frac{\nu_{np}^2 \gamma_n \nu}{(\nu_{no}^2 - \nu^2)^2 + \gamma_n^2 \nu^2} \ . \tag{12}$$

With respect to practical application, the absorption coefficient α and index of refraction n_r, given by

$$\alpha = \frac{4\pi\nu}{\sqrt{2}} \left[-\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2} \right]^{1/2} \quad \text{and} \quad n_r = \frac{1}{\sqrt{2}} \left[\varepsilon_r + \sqrt{\varepsilon_r^2 + \varepsilon_i^2} \right]^{1/2}, \tag{13}$$

respectively, provide direct relationships between calculated quantities obtained by DFT and the "conveniently measurable" quantities α and n_r. It is significant to note that in what follows, the absorption coefficient α is determined using DFT calculated spectra in the same spirit as for its measurement in the laboratory. Although permittivity functions $\varepsilon(\nu)$ are not determined explicitly in the present study, it must be kept in mind that the ultimate construction of these functions is necessary for using DFT calculated spectra to model the dielectric response of complex composite materials and associated detector designs [9].

Ground State Resonance Structure of β-HMX Water Complexes

In this section are presented the results of computational investigations using DFT concerning β-HMX water complexes. These results include the relaxed or equilibrium configuration of a single isolated molecule of β-HMX (see Table 1) and ground-state oscillation frequencies and IR intensities for this configuration, which are calculated by DFT according to the frozen phonon approximation (see Table 2). The ground state resonance structure for a single isolated molecule of β-HMX is adopted as a reference for analysis of spectral features associated with β-HMX water complexes. For these calculations geometry optimization and vibrational analysis was effected using the DFT model B3LYP [22, 23] and basis function 6-311G(2d,2p) [24, 25]. According to the specification of this basis function, (2d,2p) designates polarization functions having 2 sets of d functions for heavy atoms and 2 sets of p functions for hydrogen atoms [26]. A schematic representation of the molecular geometry of a single isolated molecule of β-HMX is shown in Fig.(1). Schematic representations of the molecular geometries of β-HMX water complexes consisting of 1, 2, 3 and 4 attached water molecules are shown in Figs. (2), (3), (4) and (5), respectively. It is significant to note that the relative positions of the attached water molecules associated with each β-HMX water complex is according to the location of stable energy minima for the relaxed or equilibrium configuration of that complex. The ground-state oscillation frequencies and IR intensities for β-HMX water complexes consisting of 1, 2, 3 and 4 attached water molecules, corresponding to its relaxed equilibrium configuration, are calculated by DFT according to the frozen phonon approximation. In the cases of 1, 2, 3 and 4 attached water molecules, these values are given in Tables 3, 4, 5 and 6, respectively. The DFT model and basis function used for these calculations are the same used for the single isolated molecule of β-HMX. As demonstrated in this study, with respect to DFT calculations concerning water complexes, it is important to note that the atomic positions of the relaxed or equilibrium configuration of a single isolated molecule, e.g., Table 1, provide a convenient starting point.

Proceeding, shown in Figs. (6), (7), (8), (9) and (10) are calculated IR intensities for a single isolated molecule of β-HMX and β-HMX water complexes consisting of 1, 2, 3 and 4 attached water molecules, respectively. The IR intensities shown in these figures are given in the form of continuous spectrum representations of the spectra. Comparison of these figures shows relative changes of intensities for individual resonances for the water complexes relative to the single molecule. These changes are physically consistent with changes of intramolecular modes resulting from water attachment. The continuous spectra shown in Figs. (6), (7), (8), (9) and (10) are constructed using a superposition of essentially Lorenzian functions of various heights and widths, which have been fit to the discrete spectra given in Tables 2, 3, 4, 5 and 6, respectively. This construction is applied within the GAUSSIAN program [12].

Finally, shown in Figs. (11), (12) and (13) are comparisons of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex having 1 attached water molecule, for a single water molecule, and for a single molecule of β-HMX. These comparisons represent an example of the correlation between single molecule resonance modes and those of a given explosive water complex. The type of comparisons shown in Figs. (11), (12) and (13) should provide insight concerning the nature of inter- and intramolecular coupling associated with a specific water complex structure. The DFT calculated absorption spectra for an isolated water molecule are given in Table 6.

Discussion

The DFT calculated absorption spectra given in Tables 3, 4, 5 and 6 provide two types of information for general analysis of dielectric response. These are the ground state resonance frequencies and estimates of molecular level dielectric response. The construction of permittivity functions using the DFT calculated absorption spectra follows the same procedure as that applied for the construction of permittivity functions using experimentally measured absorption spectra, but with the addition of certain constraint conditions. Accordingly, construction of permittivity functions using either DFT or experimentally measured absorption spectra requires parameterizations that are in terms of physically consistent analytic function representations such as the Drude-Lorentz model. Although the formal structure of permittivity functions constructed using DFT and experimental measurements are the same, their interpretation with respect to parameterization is different for each case.

The construction of permittivity functions using experimental measurements defines an inverse problem where resonant locations, peaks and widths, as well as the number of resonances, are assumed adjustable. Following this approach, it follows that many of the detailed characteristics of resonance structure are smoothed or averaged. In addition, measurement artifacts associated with sample preparation and detector configuration can in principle introduce errors. One advantage of permittivity functions constructed using experimental measurements, however, is that many aspects of dielectric response on the macroscale that are associated with multiscale averaging and molecule-lattice coupling are taken into account inherently. Accordingly, the disadvantage of this approach is that the nature of any multiscale averaging and resonant structure, contributing to dielectric response on the macroscopic level, may not be understood. This lack of quantitative understanding can in principle inhibit the development of methodologies for selective excitation of molecular modes, which are for the purpose of enhanced signature detection. Better interpretation of dielectric response of explosives on a macroscale can be achieved through correlation of resonance structure, which is experimentally observed, with spectra calculated by DFT. In principle, correlation of resonance structure would include the quantitative analysis of changes in signature features associated with the transition of the system from that of a low-density system of uncoupled molecule to that of systems consisting of molecules coupled to their molecular environment. Among these types of systems are molecular clusters of explosive molecules or individual explosive molecules having intermolecular coupling with their ambient environment, consisting of either bulk systems or individual molecules, which would include water complexes.

One approach for the construction of permittivity functions using DFT calculations, discussed previously [10,11], is that of a direct problem approach where dielectric response is estimated within the bounds of relatively well-defined adjustable parameters. Following this approach, a permittivity function is constructed using the DFT calculated absorption spectra under the condition that the calculated resonance locations are fixed, while resonance widths and number densities are assumed adjustable. With respect to this approach, reference is again made to Figs. (6), (7), (8), (9) and (10), which show continuous spectra consisting of a superposition of essentially Lorenzian functions of various heights and widths, constructed using discrete spectra. Although the primarily purpose of this type of construction within GAUSSIAN is for the purpose of enhanced visualization of spectral features, it is significant to note that this operation represents, at some level, a zeroth-order estimation of the characteristic scaling and widths of resonances contributing the dielectric response, i.e., permittivity function. For qualitative comparison of spectral features this type of zeroth-order estimate should be sufficient. For the construction of permittivity functions to be used for quantitative simulations, it is more appropriate, however, to assume the characteristic scaling and widths of DFT calculated resonances as adjustable parameters, i.e., parameters to be assigned values according to additional information.

Following an approach for construction of permittivity functions using DFT, which assumes the characteristic scaling and widths of resonances as adjustable parameters, inverse methods of analysis can be adopted. Accordingly, permittivity functions can be constructed using bin-averaged DFT calculated spectra. Given bin-averaged DFT spectra, permittivity functions can be constructed using superpositions of Lorenzian functions that are in terms of reduced sets of phenomenological scaling and widths of resonances. This approach should consider, in principle, the sensitivity of reflectivity, as would be measured by a specific detection design (see reference [9]), with respect to level of bin averaging and variation in values of the associated phenomenological scaling and widths of resonances.

It must be emphasized again, as in previous studies [10,11], that one purpose of DFT calculated spectra, related to practical application and extremely important for interpretation of signature features and the design of detectors, is the quantitative analysis of the inherent limitation on levels of detection associated with various types of detection strategies. With respect to the purpose of examining inherent limitations on IED detection, the dominant features of response spectra that are calculated using DFT provide a foundation for establishing what level of detection is achievable in the absence of instrumental and environmental factors associated with detection. Accordingly, the approach presented here, for construction of permittivity functions, provides a specific application of DFT. For any given energetic material and frequency range of the incident electromagnetic wave, DFT can calculate a set of response signatures that are each characterized by an excitation frequency, magnitude and width. These response signatures must then be adjusted parametrically to construct permittivity functions. Accordingly, parameter adjustment with respect to a given set of experimental measurements, which would entail parameter optimization and sensitivity analysis, will determine what types of signature structure are recoverable at the level of detection for a given detector design.

Finally, the DFT calculations presented here were performed using the DFT software GAUSSIAN. With respect to the approach presented here for construction of permittivity functions, these calculations represent results of numerical experiments with the “numerical apparatus” GAUSSIAN, which has associated with it specific discrete numerical representations and associated approximations. Again, an underlying factor supporting the construction of permittivity functions using DFT calculated spectra is that the associated software technology has evolved to a point of maturity where dielectric response to electromagnetic excitation can be determined quantitatively for large molecular systems.

Conclusion

The calculations of ground state resonance structure associated with β-HMX water complexes using DFT are meant to serve as reasonable estimates of molecular level response characteristics, providing interpretation of dielectric response features, for subsequent adjustment relative to experimental measurements and additional constraints based on molecular structure theory. With respect to spectroscopic methods for the detection of explosives, i.e., different types of detection strategies and their associated algorithms for post-processing of measurements, the calculated resonance spectra presented here serve the purpose of simulating detector designs for detection of water complexes of explosives. That is to say, for detection of spatially distributed water complexes of explosives, these spectra can be assumed as a reasonable estimate of dielectric response for purposes of the practical detection.

Acknowledgement

This work was supported by the Office of Naval Research.

References

[1] B. M. Rice and C. F. Chabalowski, "Ab Initio and Nonlocal Density Functional Study of 1,3,5-Trinitro-s-triazine (RDX) Conformers,``J. Phys. Chem., **101**, 8720 (1997).

[2] Y. Chen, H. Liu, Y. Deng, D. Schauki, M. J. Fitch, R. Osiander, C. Dodson, J. B. Spicer, M. Shur, and X.-C. Zhang, “THz spectroscopic investigation of 2,4-dinitrotoluene,” Chemical Physics Letters, **400**, 357-361 (2004).

[3] D. G. Allis, D. A. Prokhorova, and T. M. Korter, “Solid-State Modeling of the Terahertz Spectrum of the High Explosive HMX,” J. Phys. Chem. A., **110**, 1951-1959 (2006).

[4] D.G. Allis and T. M. Korter, “Theoretical Analysis of the Terahertz Spectrum of the High Explosive PETN,” Chem. Phys. Chem., **7**, 2398 (2006).

[5] J. Chen, Y. Chen, H. Zhao, G. J. Bastiaans, and X.-C. Zhang, Opt. Exp., **15**, 11763 (2007).

[6] M.R. Leahy-Hoppa, M.J. Fitch, X. Zheng, L.M. Hayden, and R. Osiander, “Wideband terahertz spectroscopy of explosives,” Chemical Physics Letters **434**, 227-230 (2007).

[7] J. Hooper, E. Mitchell, C. Konek, and J. Wilkinson, “Terahertz spectroscopy techniques for explosives detection,” Chem. Phys. Lett., **467**, 309 (2009).

[8] M.R. Leahy-Hoppa, M.J. Fitch, and R. Osiander,“Terahertz spectroscopy techniques for explosives detection,” Anal. Bioanal. Chem., **395**, 247 (2009).

[9] A. Shabaev, S. G. Lambrakos, N. Bernstein, V. L. Jacobs and D. Finkenstadt, “A General Framework for Numerical Simulation of Improvised Explosive Device (IED)-Detection Scenarios Using Density Functional Theory (DFT) and Terahertz (THz) Spectra,” Appl. Spectroscopy, **65**, 409 (2011).

[10] A. Shabaev, S.G., Lambrakos, N. Bernstein, V. Jacobs, D. Finkenstadt, “THz Dielectric Properties of High Explosives Calculated by Density Functional Theory for the Design of Detectors,” Journal of Materials Engineering and Performance, DOI: 10.1007/s11665-011-9857-8, 20 (9), 2011, p.1536.

[11] L. Huang, A. Shabaev, S.G. Lambrakos, N. Bernstein, V. Jacobs, D. Finkenstadt, L. Massa, “Dielectric Response of High Explosives at THz Frequencies Calculated Using Density Functional Theory,” Journal of Materials Engineering and Performance, 2011, DOI: 10.1007/s11665-011-0020-3.

[12] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B.

Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford CT, 2009.

[13] A. Frisch, M. J. Frisch, F. R. Clemente and G. W. Trucks, *Gaussian 09 User's Reference*, Gaussian Inc., 2009, p, 105-106, online: www.gaussian.com/g_tech/g_ur/g09help.htm

[14] P. Hohenberg and W. Kohn, "Inhomogeneous Electron Gas" Phys. Rev. **136**, B864, (1964).

[15] W. Kohn and L. J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects" Phys. Rev. **140**, A1133 (1965).

[16] R.O. Jones and O. Gunnarson, "The density functional formalism, its applications and prospects" Rev. Mod. Phys. **61**, 689 (1989).

[17] W.W. Hager and H. Zhang, "A survey of nonlinear conjugate gradient methods," Pacific J. Optim., 2, p. 35-58 (2006).

[18] R. M. Martin, *Electronic Structures Basic Theory and Practical Methods*, Cambridge University Press, Cambridge 2004, p. 25.

[19] E. B. Wilson, J. C. Decius and P. C. Cross, *Molecular Vibrations* (McGraw-Hill, New York, 1955).

[20] J.W. Ochterski, "Vibrational Analysis in Gaussian," help@gaussian.com, 1999.

[21] C. A. D. Roeser and E. Mazur, "Light-Matter Interactions on Femtosecond Time Scale" in *Frontiers of Optical Spectroscopy*, eds. B. Di Bartolo and O. Forte, NATO Science Series v. 168 p. 29, Kluwer Academic Publishers, Dordrecht – Norwell, 2005; C. F. Bohren and D. R. Huffman, *Absorption and Scattering of Light by Small Particles* (Wiley-VCH Verlag, Weinheim, 2004).

[22] A. D. Becke, "Density-functional Thermochemistry. III. The Role of Exact Exchange", *J. Chem. Phys.* **98**, 5648-5652 (1993).

[23] B. Miehlich, A. Savin, H. Stoll and H. Preuss, "Results Obtained with the Correlation Energy Density Functionals of Becke and Lee, Yang and Parr", Chem. *Phys. Lett.* **157**, 200-206 (1989).

[24] A. D. McLean and G. S. Chandler, "Contracted Gaussian-basis sets for molecular calculations. 1. 2nd row atoms, Z=11-18," *J. Chem. Phys.*, **72** 5639-48 (1980).

[25] T. Clark, J. Chandrasekhar, G. W. Spitznagel and P. V. R. Schleyer, "Efficient diffuse function-augmented basis-sets for anion calculations. 3. The 3-21+G basis set for 1st-row elements, Li-F," *J. Comp. Chem.*, **4** 294-301, (1983).

[26] M. J. Frisch, J. A. Pople and J. S. Binkley, "Self-Consistent Molecular Orbital Methods. 25. Supplementary Functions for Gaussian Basis Sets," *J. Chem. Phys.*, **80** (1984) 3265-69.

Table 1. Atomic positions of single isolated molecule of β-HMX (Å) after geometry optimization.

Atomic number	X	Y	Z	Atomic number	X	Y	Z
8	-2.479112	0.808262	-3.020958	7	-0.07341	-1.387792	0.284398
8	-3.388653	-0.748745	-1.789495	7	0.84757	-2.298077	-0.230144
8	-0.562157	2.824754	1.293043	6	-0.230216	0.756036	-1.562353
8	-1.864476	2.458008	-0.425286	6	-1.336694	-1.24711	-0.390367
8	2.479112	-0.808262	3.020958	6	0.230216	-0.756036	1.562353
8	3.388653	0.748745	1.789495	6	1.336694	1.24711	0.390367
8	0.562157	-2.824754	-1.293043	1	0.707094	0.321983	-1.911618
8	1.864476	-2.458008	0.425286	1	-0.585747	1.484863	-2.287392
7	-2.458383	-0.034644	-2.142016	1	-1.644269	-2.203497	-0.804192
7	-1.252463	-0.269474	-1.491636	1	-2.080295	-0.92493	0.340903
7	0.07341	1.387792	-0.284398	1	-0.707094	-0.321983	1.911618
7	-0.84757	2.298077	0.230144	1	0.585747	-1.484863	2.287392
7	2.458383	0.034644	2.142016	1	1.644269	2.203497	0.804192
7	1.252463	0.269474	1.491636	1	2.080295	0.92493	-0.340903

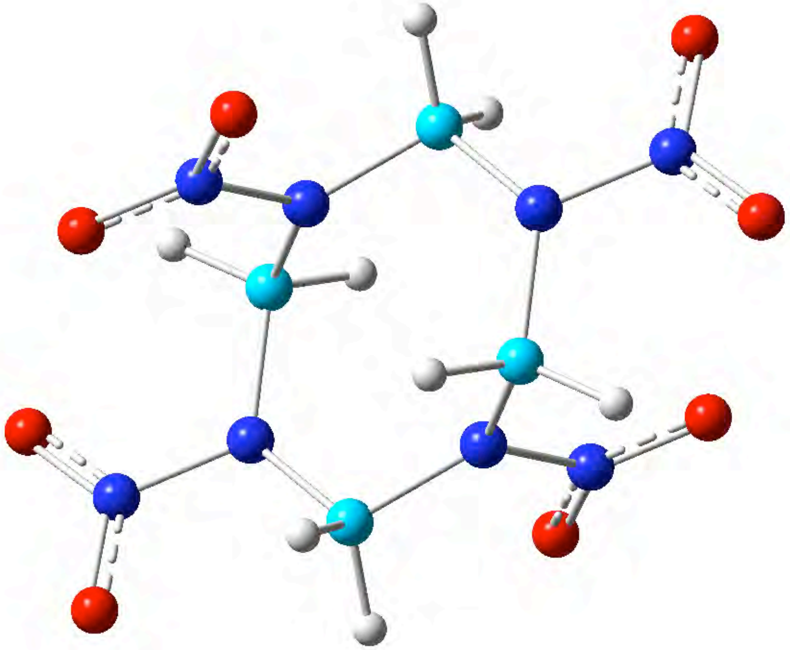

Figure 1. Molecular geometry of single isolated molecule of β-HMX.

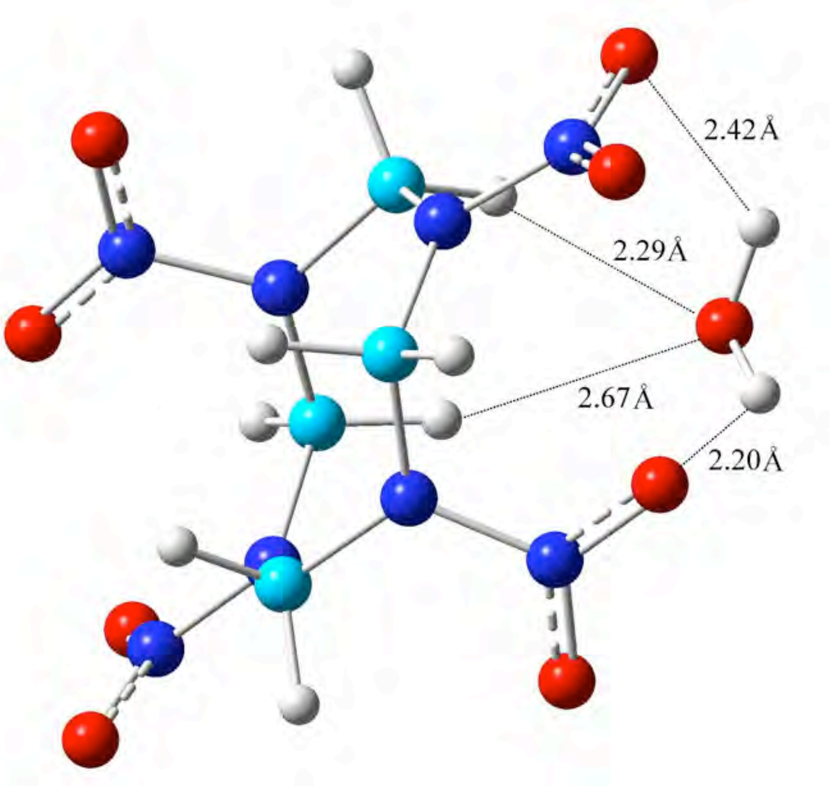

Figure 2. Molecular geometry of β-HMX water complex consisting of 1 attached water molecule.

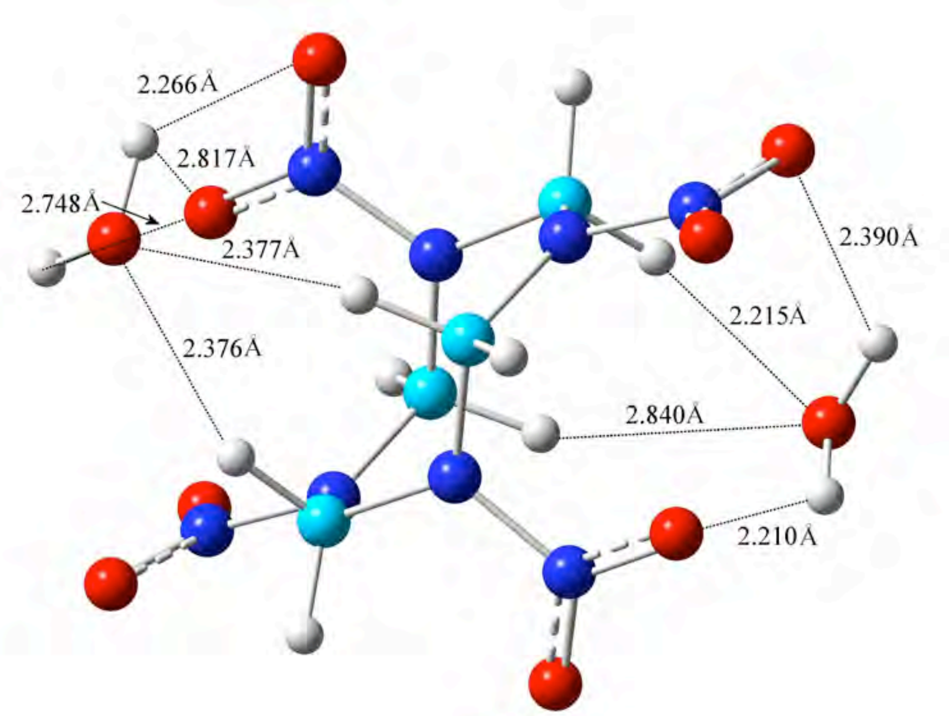

Figure 3. Molecular geometry of β-HMX water complex consisting of 2 attached water molecules.

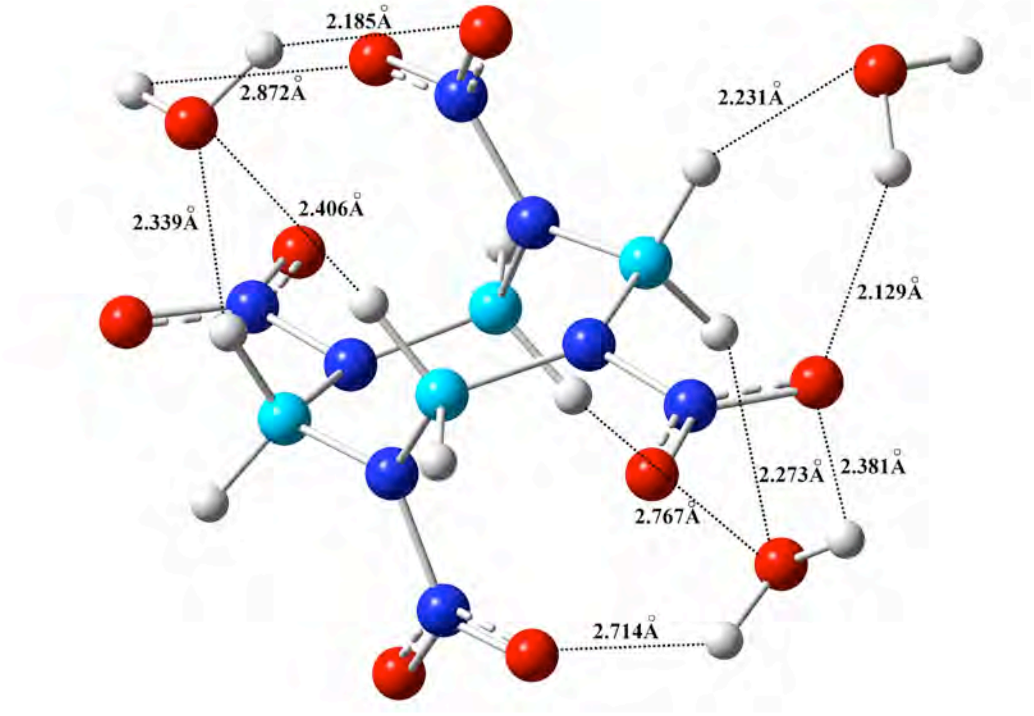

Figure 4. Molecular geometry of β-HMX water complex consisting of 3 attached water molecules.

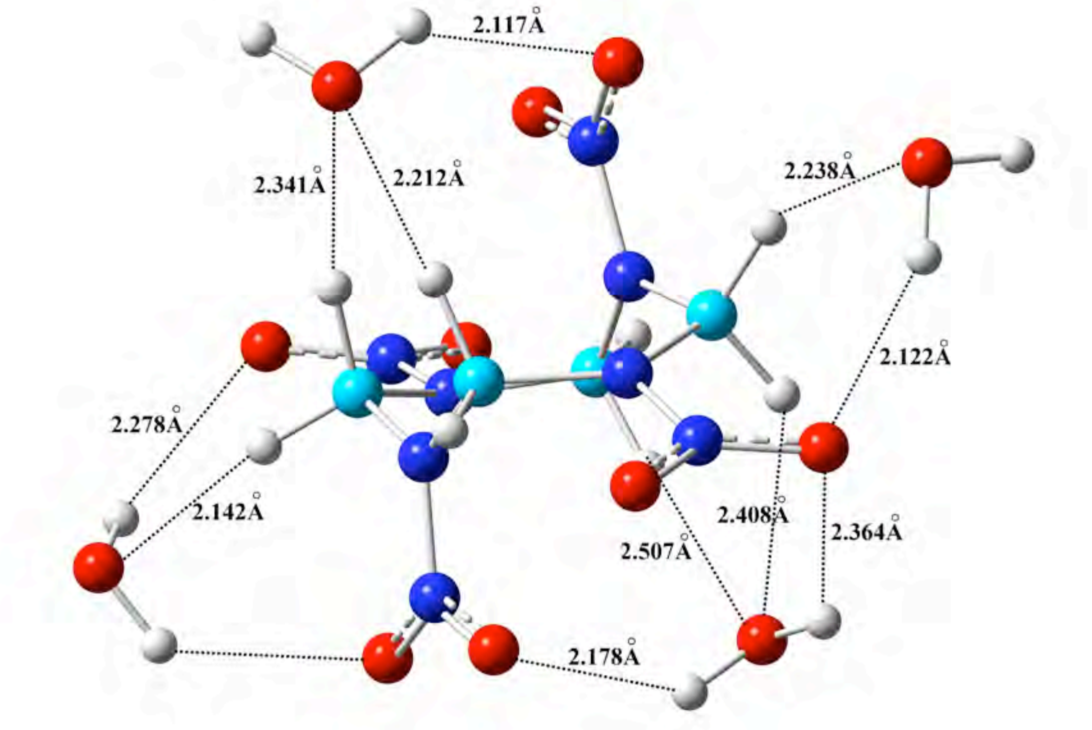

Figure 5. Molecular geometry of β-HMX water complex consisting of 4 attached water molecules.

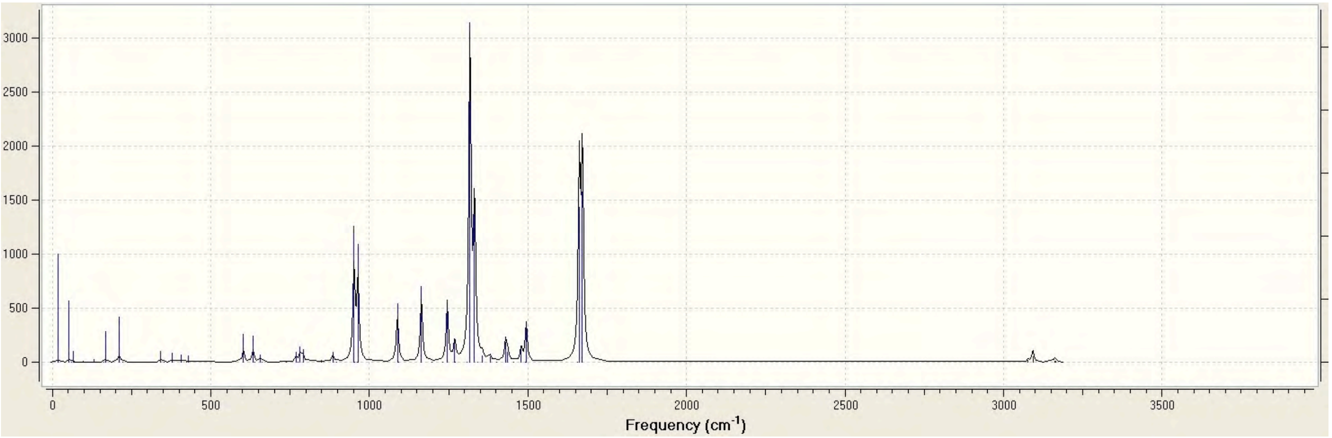

Figure 6. Continuous-spectrum representation of IR intensity (arbitrary units) as a function of frequency calculated using DFT for single isolated molecule of β-HMX.

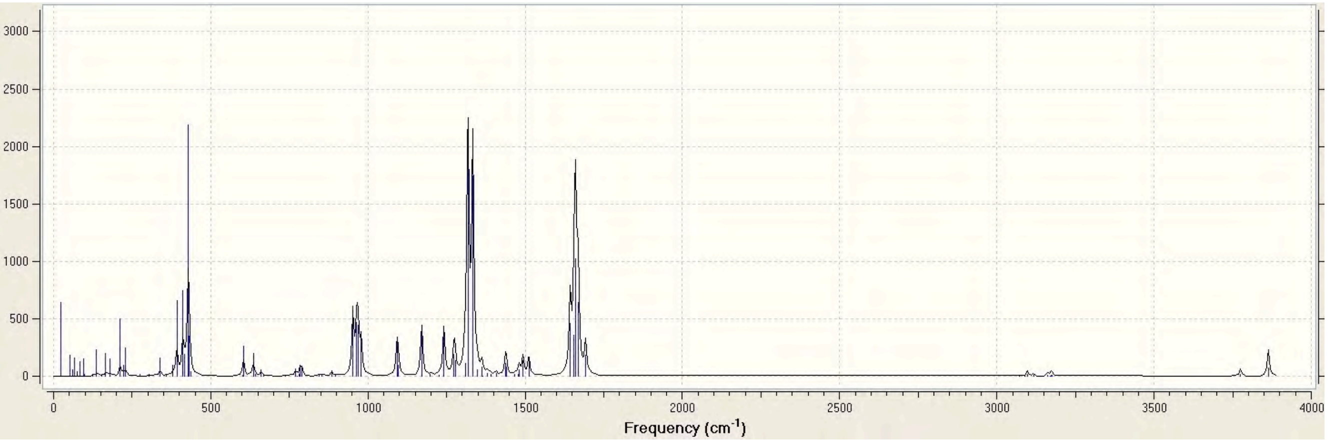

Figure 7. Continuous-spectrum representation of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex consisting of 1 attached water molecule.

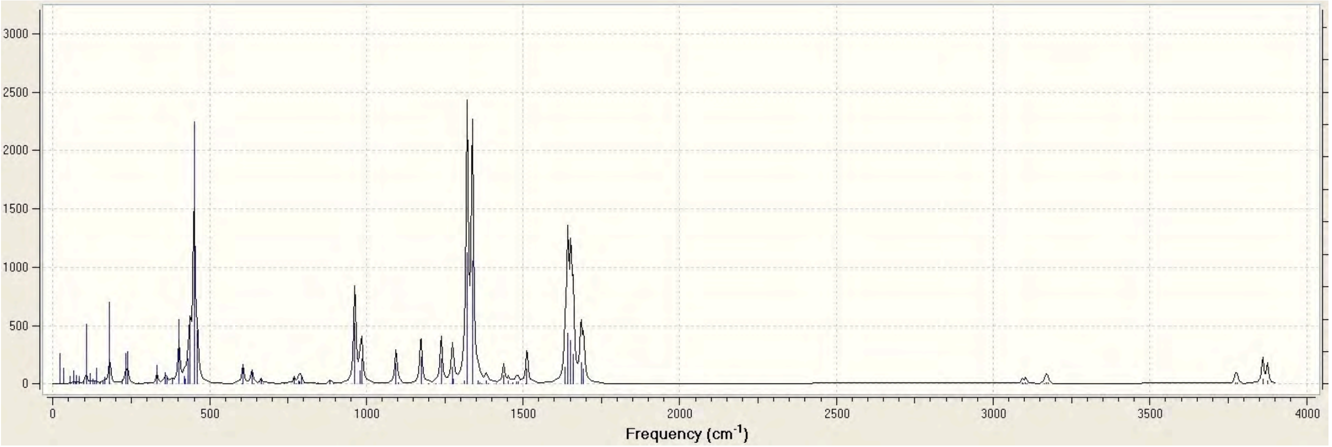

Figure 8. Continuous-spectrum representation of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex consisting of 2 attached water molecules.

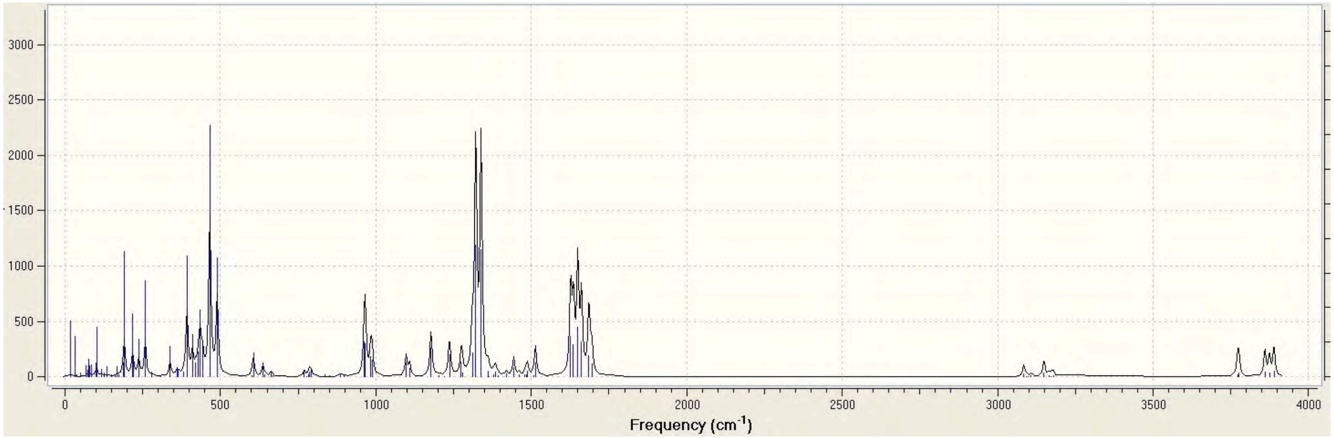

Figure 9. Continuous-spectrum representation of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex consisting of 3 attached water molecules.

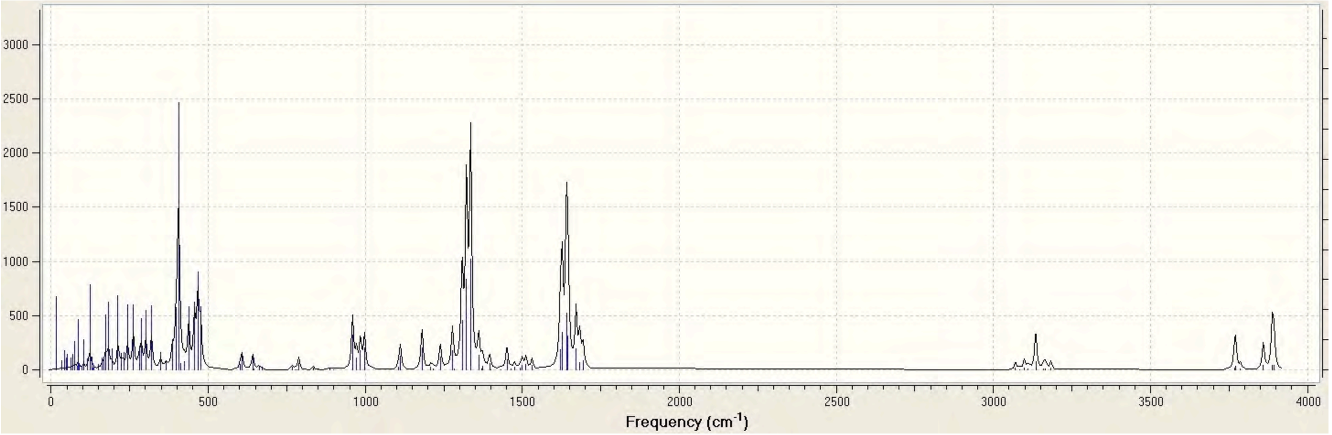

Figure 10. Continuous-spectrum representation of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex consisting of 4 attached water molecules.

Table 2. IR intensity as a function of frequency for a single isolated molecule of β-HMX.

Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
18.0302	3.8738	656.8692	9.2653	1331.7427	426.2797
53.2212	6.4573	661.8475	0.0000	1343.2512	0.0000
61.9072	0.0000	738.4334	0.0000	1356.3191	16.8980
67.1865	1.4375	768.5782	15.3857	1357.3042	0.0000
68.4887	0.0000	774.3588	0.0000	1380.5103	14.4161
91.4604	0.0000	781.8836	24.3877	1380.9347	0.0000
97.0024	0.2151	781.9183	0.0000	1402.7491	0.0000
119.4615	0.0000	790.6682	19.2817	1429.9025	57.3480
130.1859	0.5830	849.4091	0.0000	1436.4362	27.8791
162.0471	0.0000	849.4226	3.3150	1455.2174	0.0000
167.7281	10.0649	884.5014	17.3546	1477.3986	0.0000
211.0685	18.8994	896.0556	0.0000	1479.2684	39.9261
221.0217	0.0000	951.5063	257.8989	1491.2864	0.0000
272.8039	0.0000	952.4117	0.0000	1494.7878	105.2168
300.6558	0.0000	963.0203	0.0000	1657.0037	0.0000
342.0961	7.5711	963.9386	225.5511	1662.1891	512.3396
352.9131	0.0000	1088.4111	127.2236	1670.6206	0.0000
377.2932	6.7134	1092.0485	0.0000	1671.9207	565.9194
405.6983	0.0000	1164.1815	174.3309	3076.7251	0.0000
407.3339	5.8638	1198.3514	0.0000	3077.9143	8.8042
424.2884	0.0000	1231.2358	0.0000	3092.8662	31.2866
427.9083	5.1902	1245.8247	154.3702	3093.2776	0.0000
600.8529	0.0000	1269.5238	54.6922	3160.9194	0.0000
603.1155	33.7774	1270.5952	0.0000	3161.0083	6.5753
633.4601	32.6639	1309.1761	0.0000	3164.0520	5.6130
638.6084	0.0000	1317.1750	890.8273	3164.2056	0.0000

Table 3. IR intensity as a function of frequency for β-HMX water complex consisting of 1 attached water molecule.

Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
24.1002	3.8902	604.5654	39.5762	1333.1212	582.802
51.8614	2.3862	635.1459	31.7445	1346.9714	20.5648
60.6607	0.8514	640.9821	3.3589	1362.2961	28.2644
65.6949	2.622	660.1198	9.7647	1364.5699	1.4856
75.7486	0.8409	666.839	1.561	1380.2231	9.2992
83.2691	2.6673	737.7764	0.297	1390.1044	5.0315
95.1884	3.7302	769.4102	12.4888	1407.7133	8.6185
98.1955	0.3886	775.445	0.3217	1437.1622	40.0784
123.4485	0.6731	782.4214	3.8228	1440.1871	28.418
125.0094	0.4632	784.887	18.8291	1466.4492	5.3808
137.3152	7.8425	790.8389	16.8824	1477.8206	6.6037
153.2288	0.5863	845.7614	2.8712	1481.1555	22.6132
166.0786	8.2841	853.0252	3.5655	1493.1495	51.5029
179.7288	6.8467	884.1751	10.671	1511.3824	50.9297
212.3214	26.7954	895.9258	2.4405	1643.2549	188.5507
221.979	5.3774	952.1349	146.8456	1655.3878	148.4476
229.8232	14.0949	963.763	112.6515	1659.7448	426.8192
275.9215	1.3288	968.4082	108.4028	1668.1786	267.8376
304.7264	1.6285	978.058	84.5182	1692.1395	78.9668
339.5692	13.5263	1092.5094	87.7999	3070.2251	5.9443
357.8799	1.4648	1097.1985	26.0934	3090.0718	1.0618
378.6804	8.8919	1170.851	131.199	3097.21	12.9463
392.2732	64.9746	1198.6416	4.4515	3116.512	6.6892
410.8942	77.1145	1227.0546	2.5669	3160.9563	7.3941
416.8799	19.7146	1241.4521	123.3436	3169.0471	1.7585
428.4187	234.5501	1273.262	61.7217	3172.7981	5.1295
430.2787	37.9977	1277.0394	43.9799	3175.7937	10.655
436.4843	4.9058	1308.9626	36.682	3774.9387	20.0244
602.3002	1.4626	1317.7758	651.5803	3863.5928	68.7926

Table 4. IR intensity as a function of frequency for β-HMX water complex consisting of 2 attached water molecules.

Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
21.9879	2.5735	450.1299	456.5264	1338.3352	634.258
34.3453	2.1649	460.6721	94.7163	1356.4965	16.363
53.1618	1.6079	602.5043	1.0009	1362.6941	4.7779
66.6503	3.4464	606.0327	46.3881	1367.0192	0.8126
71.0185	0.3122	634.7177	35.3106	1382.0059	16.6388
75.2511	2.5662	642.1107	1.4034	1387.8292	4.0811
83.8138	2.4767	664.3633	13.3205	1413.8153	1.3449
96.8735	1.3187	670.2267	0.7536	1438.1053	46.1386
105.847	24.486	736.2117	0.0485	1453.9474	16.2966
119.3245	4.8907	770.1874	17.5689	1468.5138	4.9246
127.9235	2.5682	775.9007	0.1639	1477.9954	14.5034
133.8538	1.5047	784.1656	9.8549	1485.2114	14.7303
139.6037	8.5059	785.9433	7.9348	1509.3254	0.0473
152.1325	1.0905	791.5823	20.3684	1512.4072	89.598
160.2546	1.8673	844.4958	3.0078	1634.7401	105.5441
166.1967	4.5278	852.2977	1.0912	1642.8118	321.8763
179.7118	3.7931	883.4888	9.7414	1652.2354	276.216
181.2411	57.4443	896.0809	0.9495	1659.9137	189.494
220.5229	3.5582	961.6681	25.0898	1684.9586	137.5911
232.3472	27.4048	963.273	226.6027	1693.2728	99.9029
238.6945	29.7656	979.8994	49.448	3093.1897	10.9345
274.7935	0.9694	985.6424	94.3341	3096.1335	0.6565
303.2299	0.9406	1094.5587	86.6952	3103.4895	11.6298
332.2694	24.1007	1103.3862	5.0064	3106.7854	6.8798
358.0105	15.2304	1174.0201	123.7111	3164.0762	5.2258
363.684	9.8359	1199.8951	2.75	3168.6411	4.4807
380.3188	6.8743	1223.5364	3.513	3168.8345	12.9711
401.9715	99.5211	1238.8508	119.5841	3174.0332	15.999
418.5351	11.6812	1274.0492	83.652	3772.9968	19.9998
421.2038	7.9571	1278.6814	22.3861	3779.0583	20.7382
431.189	42.5398	1311.401	15.8506	3860.3142	67.201
437.5174	114.3354	1321.6049	669.1733	3875.4561	48.2709

Table 5. IR intensity as a function of frequency for β-HMX water complex consisting of 3 attached water molecules.

Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
18.9755	3.8354	428.5766	38.3644	1338.2919	617.9783
31.2391	4.5621	434.7118	105.4045	1360.3617	29.8608
37.1532	0.2436	442.633	57.5679	1364.5444	1.9942
49.0583	0.7008	465.8682	424.8449	1379.7704	12.0041
68.2147	2.6898	489.5334	211.3416	1385.5096	22.5194
72.8153	1.7551	602.474	1.3882	1394.818	5.3666
77.2412	4.9193	605.9666	51.7556	1419.1786	12.5563
78.4375	3.1059	636.7745	31.2824	1443.3724	49.1585
85.3311	3.5781	643.6578	4.8512	1460.0256	11.759
99.635	4.902	663.5213	12.3182	1477.8167	8.4476
102.9422	18.4121	669.7303	1.408	1484.0685	9.5899
118.9333	3.3402	735.6577	0.2536	1487.6165	29.9619
126.0984	1.9291	770.2205	16.0818	1509.0251	8.0182
134.5519	4.9675	776.343	0.1624	1513.5226	75.8264
136.5644	2.9298	783.7203	5.1795	1626.7344	237.9782
149.7814	1.1946	786.2168	13.445	1635.5948	192.5735
160.9185	0.5476	791.1068	18.1227	1649.4012	298.0874
167.9494	6.1066	837.0082	4.566	1661.4939	209.7054
171.9333	1.4386	851.8101	2.4475	1685.1886	129.8862
186.659	9.2848	885.0266	6.7654	1685.3098	56.1783
190.9049	86.4193	897.1925	3.9976	1694.4594	82.0129
217.0587	49.9255	963.3241	121.5914	3084.0237	32.0339
220.1223	15.2783	966.1639	116.7309	3092.2666	3.2476
237.0691	32.5519	983.5465	73.6771	3096.6829	1.1631
237.6609	15.0183	988.2074	59.9494	3106.6775	8.0044
258.3627	90.317	1097.3689	55.7823	3149.1528	44.002
277.4441	5.1376	1108.4871	33.7716	3164.9399	8.9413
307.7503	0.4963	1177.4404	121.854	3171.0754	3.962
338.147	36.8821	1202.0184	3.0815	3178.8337	15.8527
359.9598	12.4291	1219.5153	2.0522	3771.3279	19.7381
364.6954	8.7314	1236.6637	98.3756	3772.4429	25.0106
381.6116	6.9501	1274.7211	69.0751	3775.7112	48.8176
392.3634	171.3429	1279.2181	15.6458	3859.5813	70.2806
409.7918	62.3359	1310.0735	112	3874.1377	56.3632
420.0597	20.6097	1321.2195	629.3669	3888.5754	80.0995

Table 6. IR intensity as a function of frequency for β-HMX water complex consisting of 4 attached water molecules.

Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)	Frequency (cm^{-1})	Intensity (km/mol)
17.5096	5.3217	405.2346	451.4603	1335.4362	618.0751
32.2671	1.2413	413.2187	11.0599	1361.2402	84.0975
41.4207	3.3001	423.1875	1.7429	1372.109	8.5776
48.7948	2.5497	423.6939	14.4517	1373.629	23.8396
51.7418	3.4705	437.6172	115.2926	1395.983	36.4484
63.3594	3.2355	456.0788	129.3022	1400.3528	0.679
69.5541	4.441	466.6453	191.4106	1432.0717	3.7114
74.2101	8.9462	475.5214	126.0174	1450.9781	62.402
84.3141	1.3032	602.6583	14.1419	1465.0052	7.1999
85.8377	18.0333	608.2344	41.8307	1475.9679	17.7902
89.0411	1.6217	641.5942	39.5861	1492.4049	10.4544
96.9849	1.7454	644.3347	3.8757	1499.8677	29.6739
103.0207	12.9132	661.9204	10.8272	1511.6793	33.9154
116.3967	5.4718	672.4523	4.4992	1531.2382	28.0786
122.6234	43.6076	736.981	1.8848	1621.1953	139.245
129.8889	6.9922	768.6489	10.3123	1626.7458	256.1473
132.4933	0.9631	775.9567	0.9879	1640.3615	386.6965
135.8571	2.7325	781.2701	1.5846	1645.3972	235.2164
150.8562	3.4291	787.8068	22.1658	1671.2667	150.7681
162.306	8.3786	788.5076	11.1481	1681.8376	38.4593
167.099	9.2174	835.0339	8.6473	1683.8	51.6611
173.7567	39.6809	848.1108	1.6207	1693.4922	64.0081
182.224	51.6192	886.7697	4.335	3070.355	20.4395
192.6826	17.4046	898.8128	1.691	3083.2817	4.2517
212.7421	65.4224	959.5424	141.2007	3098.5474	26.0293
223.3525	15.4395	972.2538	48.0479	3111.2085	13.6722
230.5729	16.7649	984.5794	80.3823	3134.6909	106.4048
243.0139	65.8769	997.6438	92.3243	3160.3103	18.5114
261.3994	71.086	1106.2206	13.857	3166.448	19.5791
261.9303	24.3187	1111.8564	63.9654	3183.7341	22.6963
280.0666	28.3248	1180.5941	111.1448	3767.3037	31.4855
286.6704	61.6512	1208.8069	13.9502	3770.6052	18.8963
301.0446	75.0651	1217.2313	6.6802	3771.1875	58.1449
319.031	85.2519	1238.8948	67.0541	3786.9207	17.2156
348.9839	25.3278	1277.2268	102.9468	3859.4612	72.8365
365.1529	14.0613	1282.5206	6.807	3887.5127	45.7339
386.0568	46.9347	1308.196	267.7637	3888.4397	82.4459
397.536	102.73	1322.1364	497.8772	3893.4922	82.5938

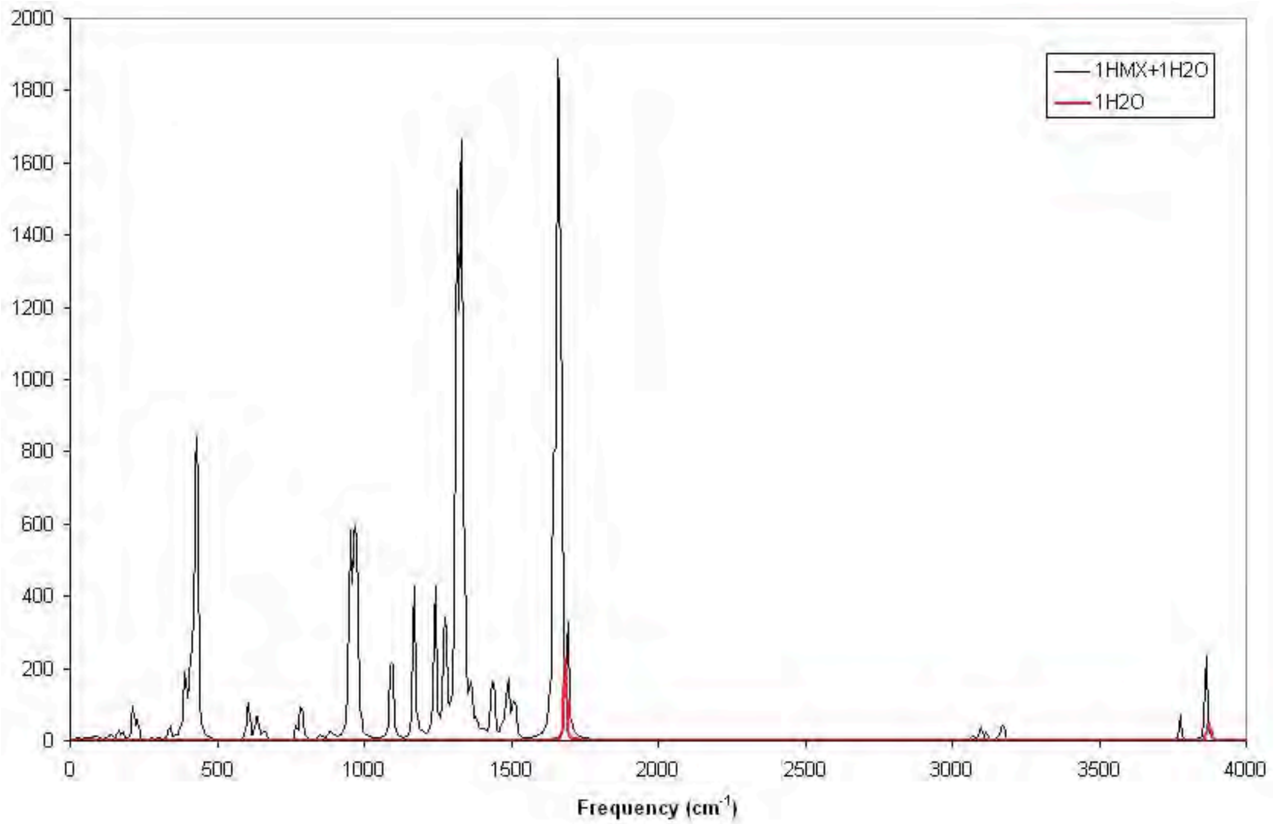

Figure 11. Comparison of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex having 1 attached water molecule and for a single water molecule.

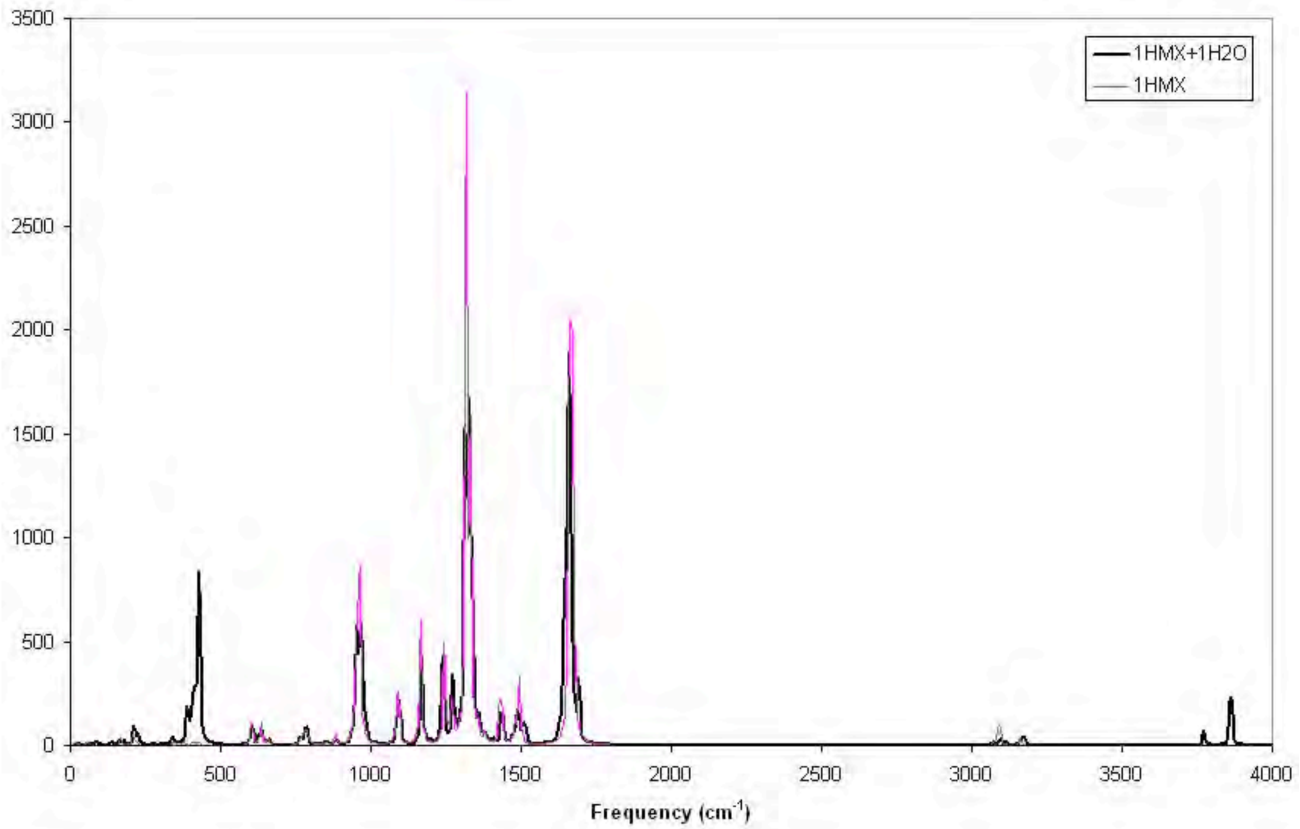

Figure 12. Comparison of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex having 1 attached water molecule and for a single molecule of β-HMX.

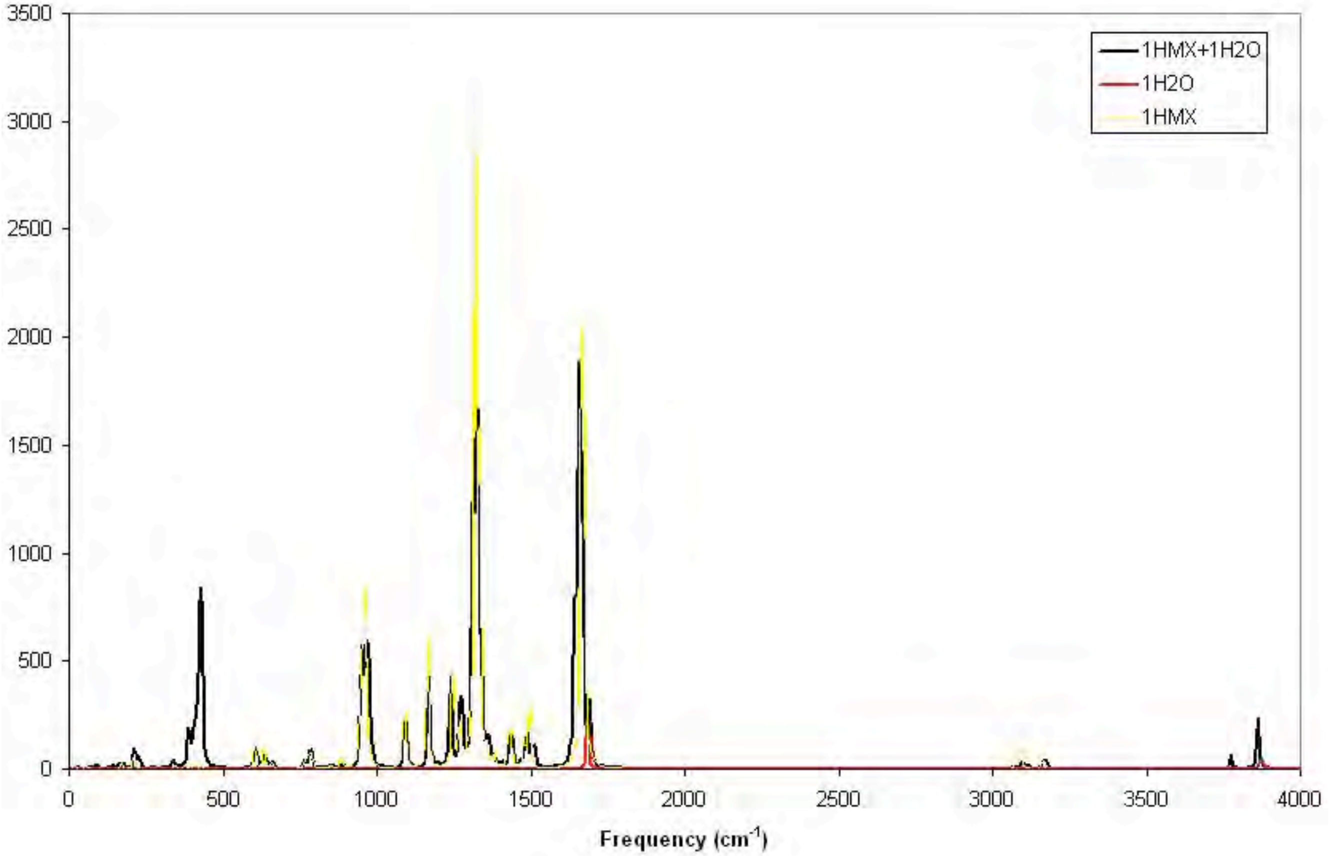

Figure 13. Comparison of IR intensity (arbitrary units) as a function of frequency calculated using DFT for β-HMX water complex having 1 attached water molecule, for a single water molecule, and for a single molecule of β-HMX.

Table 6. IR intensity as a function of frequency for isolated water molecule.

Frequency (cm^{-1})	IR Intensity (km/mole)
1685.9065	66.4511
3766.9605	1.6788
3873.7393	23.3549