

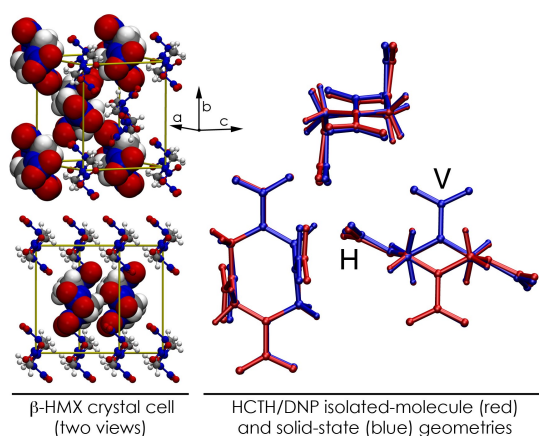
## Solid-State Modeling of the Terahertz Spectrum of the Explosive HMX

The Korter Research Group at Syracuse University in New York have used Accelrys' Density Functional Theory (DFT) program DMol<sup>3</sup> to model the solid state terahertz spectrum of the high explosive HMX<sup>1</sup>. Reporting in *J. Phys. Chem. A* (2006, 110, 1951-1959), the scientists obtained excellent agreement between experiment and solid-state theory whereas a simple molecular calculation failed to reproduce the spectral features. This latter deficiency can be attributed to crystal packing effects and hydrogen bonding in the crystal structure, which are missing in the molecular calculations.

### Introduction

Dr Damian G. Allis, Syracuse University, said, "For quantum chemists working on the property prediction of molecules and molecular crystals, productivity depends in its entirety on the availability of software that can properly address the problems they're asked to solve. DMol<sup>3</sup> proved its value to both myself and others in the neutron community years ago for the assignment of inelastic neutron scattering spectra of molecular crystals, where the intensities of modes are very easy to obtain from the calculated results."

Experimental terahertz (THz) spectroscopy investigations in the spectral range of 3-120 cm<sup>-1</sup> can be used for detection and identification for a wide assortment of compounds, since the compounds have distinct spectra 'fingerprints' in this region of the electromagnetic spectrum. THz spectroscopy is hence widely used for security applications<sup>2</sup>, and more routinely in the pharmaceutical industry<sup>3</sup>. The assignment of the observed experimental features is often difficult. In some cases, the experimental interpretation of spectra does not yield a unique assignment; a spectrum may be consistent with more than one geometric structure. Computational chemistry plays a pivotal role: by computing the spectra, the correspondence between spectral peaks and molecular or crystal features may be assigned unambiguously.



### Module used

Materials Studio - DMol<sup>3</sup>

### Industry sectors

Chemicals  
Security  
Pharmaceuticals

### Organization

Syracuse University, NY

Figure 1. Two representations of beta-HMX. left: two views of the crystal structure; right: superimposed geometries of isolated molecules (red) and solid state (blue)

### Results

The authors used Accelrys' DMol<sup>3</sup> program to interpret the THz spectrum of the most stable crystal form (beta) of the high explosive HMX. The molecular and crystal structures of beta-HMX are displayed in Fig. 1. This figure also shows a comparison of the geometries of the molecule in the gas phase and solid state.

"Terahertz and neutron spectroscopy of solid-state materials are complementary methods in many respects and share in the considerable difficulty in spectral assignments without

the proper treatment of the crystal environment. I was amazed at the level of improvement in the DMol<sup>3</sup> simulated HMX spectrum upon going from the molecular to the solid-state calculations,” said Dr Allis.

It was found that calculations using the gas phase molecular structure (Fig. 1 (right)) were unable to reproduce the experimental spectra features. If the optimized crystal structure of Fig. 1 (left) was used, however, both the agreement with the crystallographic structure and the measured THz spectrum was markedly improved. A comparison of experimental and calculated solid-state spectra is shown in Fig. 2.

The intensities of the calculated spectra in Fig. 2 were obtained using a difference-dipole calculation from a Mulliken or a Hirshfeld charge analysis, with the former generally giving better agreement with the experimental spectrum.

An analysis of the calculated normal modes displayed in Fig. 2 shows that the major features of the experimental spectrum can be assigned to optical translational modes of molecules in the crystal cell. By contrast, the majority of the spectral lines in the gas phase (not shown in Fig. 2) are shifted to much higher frequencies. The authors concluded that only by including crystal packing and intermolecular interactions can a meaningful interpretation of the THz spectrum be achieved. Therefore, it is essential to employ a solid-state program like DMol<sup>3</sup>, since a simplistic gas phase calculation of the isolated molecule cannot account for these effects.

Dr Allis continued, “The two findings that stood out immediately in the solid-state results were the degree of shifting of internal molecular modes due to crystal packing and the importance of the relative motions of molecules for the reproduction of the terahertz spectrum. For a molecule in a crystal environment, the rotational and translational modes unimportant to isolated-molecule vibrational assignments occur as relative motions between molecules, with some of these external vibrational modes being infrared-active. You clearly cannot reproduce this structure accurately (or at all!) without the crystal environment. While these relative motions may be of limited concern to higher frequency spectroscopists looking at internal molecular modes above 500 cm<sup>-1</sup> or so, these relative motions lies right in the middle of the region of the optical spectrum that terahertz spectroscopy is ideal for studying.”

This study shows that solid-state modeling can be used to advance THz spectra analysis in the pharmaceutical industry or for security screening purposes.

Dr Allis concluded, “This work on HMX was an ideal case showing that the underlying theory is itself more than adequate (certainly for the assignment of HMX) and that proper use of the theory is everything.”

“The DMol<sup>3</sup> calculations on a quad-AMD box were almost embarrassingly fast. The crystal cell geometry optimizations and normal mode analyses for each of the considered functionals were completed and analyzed in a matter of days.”

## References

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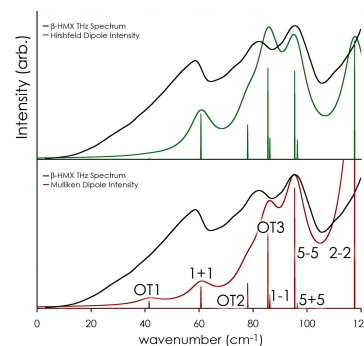


Figure 2. Predicted and experimental THz spectra of beta-HMX. Both calculated spectra were obtained using the DFT optimized crystal structure. The top spectrum was obtained using Hirshfeld dipole intensities, the spectrum in the lower panel was obtained using Mulliken dipole intensities.