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13. ABSTRACT (Maximum 200 words) Specific aims of the project: To explore the observability and observation of quantum mechanical wave functions, and the reaction pathways of highly energetic molecules. Highlights of the results: The extent of the observability of vibrational wave functions in polyatomic molecules was determined. Using pump-probe diffraction methodologies, the effect of vibrational excitation was found to be on the order of 1%, well observable using current experimental methodologies. The signatures of the vibrational excitation are found to be specific to the vibrational state, even when the vibrations are isoenergetic. Therefore, the diffraction technique is amenable to deliver three-dimensional views of the probability density distributions of vibrating molecules, potentially extending the limits with which matter can be imaged to the picometer regime. On the study of reaction pathways of energetic molecules, we extended our work on the development of multi-photon ionization via Rydberg states to quite a few molecules. We showed that the Rydberg spectra can be used to fingerprint the shape of a molecule. This discovery will have significant ramifications for analytical chemistry, as it may be possible to combine the Rydberg fingerprint technology with mass spectrometry. The technique could be applied to identify explosives in the presence of other volatile compounds. A patent has been applied for.					
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4. Statement of the problem studied

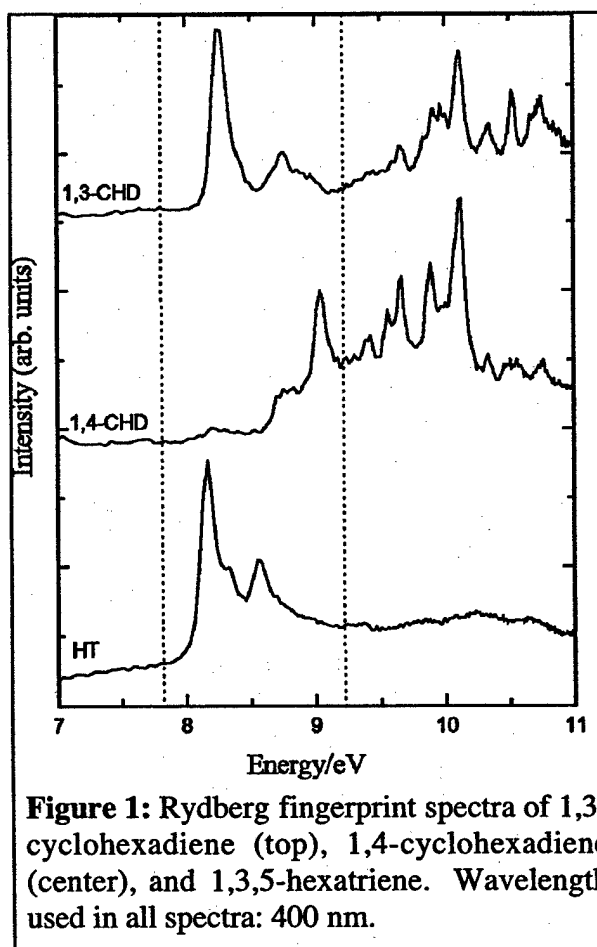
The research program has two foci. First, we explore the limits to the observability of quantum mechanical wave functions using diffraction methodology. This work has both a theoretical and an experimental component. Secondly, we investigate the reaction pathways of highly energetic and short-lived transient species. This part of the work focuses pathways of photoionization, and in particular the recently discovered role of Rydberg states in the ionization process.

5. Summary of the most important results

The project was blessed with several very nice scientific discoveries. Of particular importance was the development of a resonant, or partially resonant, multiphoton ionization scheme via superexcited states and Rydberg states, which we discovered in the previous funding period, into a tool to fingerprint molecular structures. This discovery might be of interest to the Army as a technique to detect trace gases of toxic compounds in the presence of decoy substances. The work forms the basis of a patent application, as it may have significant commercial value. We describe this discovery in the next section, followed by a description of our advances in the measurement of quantum mechanical wave functions.

Photoelectron Spectroscopy

In previous years, we have developed a technique to photoionize molecules via highly excited and superexcited valence states, and a set of molecular Rydberg states. While initial



experiments focused on phenol, subsequent work showed the scheme to work as well in toluene, cyclohexadiene, as well as other molecules. In 2002 we demonstrated that the ionization scheme can be utilized to obtain a *structure fingerprint spectrum* of the molecule. The structure specificity arises because the Rydberg spectra are sensitively dependent on the molecular structure.

As an example, figure 1 shows the Rydberg fingerprint spectra of 3 molecules, 1,3-cyclohexadiene, 1,4-cyclohexadiene, and 1,3,5-hexatriene. Those molecules are structural isomers of each other, and have almost identical mass spectra. As can be seen, the Rydberg spectra are dramatically different.

We have obtained Rydberg fingerprint spectra of other isomers as well. Specific isomeric systems that we have investigated are:

Napthalene – azulene: both $C_{10}H_8$
o-, m-, and p- fluorophenol, C_6H_5FO

The Rydberg fingerprint spectra have a number of attributes that make them very favorable for analytical applications. Specific points of interest are:

- The scheme appears to be applicable to all molecules. Any molecule that we have tried to date worked. This includes, in addition to the ones mentioned above, the molecules toluene, and indole.
- The wave function of the Rydberg state is quite large. As a result, Rydberg fingerprints are sensitive to the global molecular structure, rather than the local structures that is observed with other techniques (such as IR, NMR).
- Because of the large size of the Rydberg orbital, the technique is sensitive to structures even in large molecules. It may be possible to extend the method to nano-size clusters such as those used in catalysis, and to biological molecules (proteins).

In a potential practical implementation, the Rydberg fingerprint technology would be combined with a mass spectrometer. Such a combined instrument would output the mass of the substance on the one hand, and the Rydberg fingerprint on the other hand. This would give a multi-dimensional output in orthogonal coordinates, which would be far more specific than a simple mass spectrum. It may be possible to combine the Rydberg fingerprint technique with a mass spectrometer of small size. An implementation in a field instrument could therefore be envisioned.

Electron diffraction

The objective of this project was to determine the limits of observability of vibrational probability density distributions, the square of the wave functions, using electron diffraction. The project has a theoretical and an experimental component. From the experimental work we concluded that difference diffraction signals as small as 0.1% of the total signal are observable with pump-probe diffraction techniques. The theory shows that the signature of vibrational motions in the diffraction patterns are on the order of 1%, even if the vibrations in question are at the same energy. The conclusion is therefore that it is possible to observe vibrational probability density distributions using present-day diffraction methodology. Some of the results of this work are presented in more detail below.

Electron Diffraction – Experiments

In 2001 we published our ground-breaking results on the ultrafast time-resolved electron diffraction measurements of the electrocyclic ring opening reaction of 1,3-cyclohexadiene. In these experiments we used a 275 nm pump beam to excite the B_1 state, which subsequently decays to the ground electronic surface. The molecule breaks the ring on the ground electronic state surface. Diffraction patterns were obtained with an ultrashort electron pulse, both with the pump laser on and the pump laser off. The difference between the two patterns reflects interatomic distances that change upon laser exposure. Difference patterns were observed at various delay times in the picosecond range. The difference signals shown in figure 1 are less than 1% of the total signal. Presently, the noise floor of the experiment is at 0.1% of the total signal.

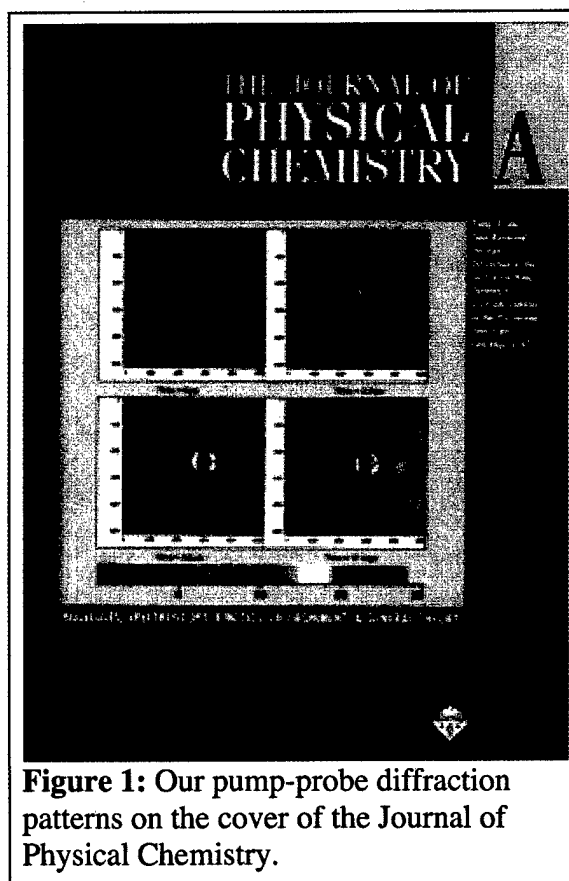


Figure 1: Our pump-probe diffraction patterns on the cover of the Journal of Physical Chemistry.

Electron Diffraction – Theory

The theoretical work focused on the s-tetrazine ($C_2H_2N_4$) molecule as a model system. With 8 atoms, this molecule can serve as a model for an honest polyatomic molecule on the one hand, but is theoretically treatable in considerable detail on the other hand. Our work included the following:

- A full ab initio calculation of the structure and normal mode displacement vectors.
- A quantum mechanical and a classical calculation of the alignment distributions that can be achieved by alignment with high intensity lasers.
- A calculation of the diffraction patterns that can be observed, as a function of alignment intensity, for ground state molecules, electronically excited molecules, and for electronically plus vibrationally excited molecules.

Figure 2 illustrates the type of results we have obtained. The figure shows the diffraction patterns of perpendicularly laser-aligned s-tetrazine, in comparison to the limiting case of partially clamped molecules. Top panel, clamped at ($\theta = 90^\circ$, $\phi = 0^\circ$), with χ isotropic: this implies that the plane of the molecule is fixed, but that the molecule is free to rotate within the plane. Bottom panel, aligned in the y,z -plane by a circularly polarized laser pulse with 9.56×10^{12} W/cm². From the calculation we learn that at a detector direction of 90° , the pattern from aligned molecules faithfully represents that of a clamped molecule, while in perpendicular direction there is a significant deviation. This kind of information will greatly aid experimental work on aligned molecules.

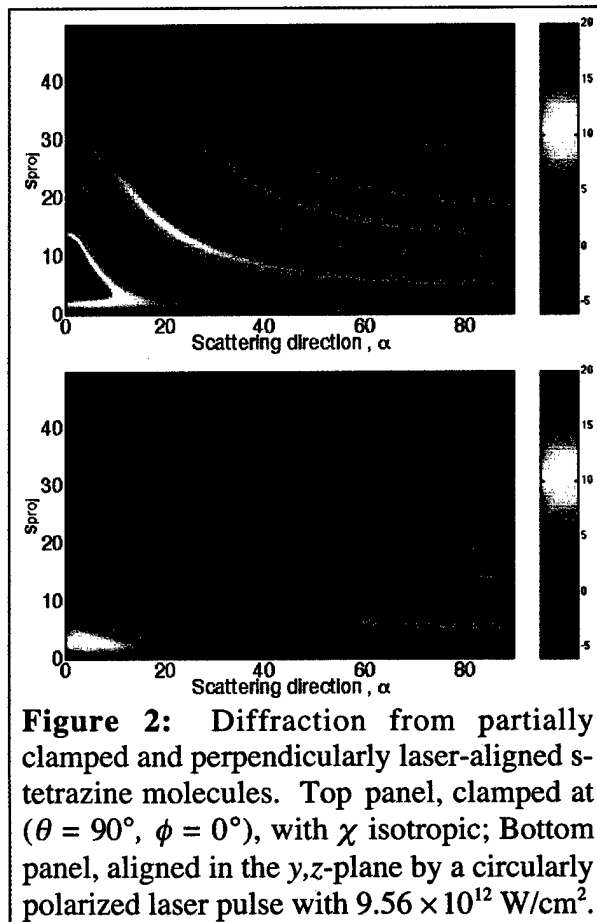
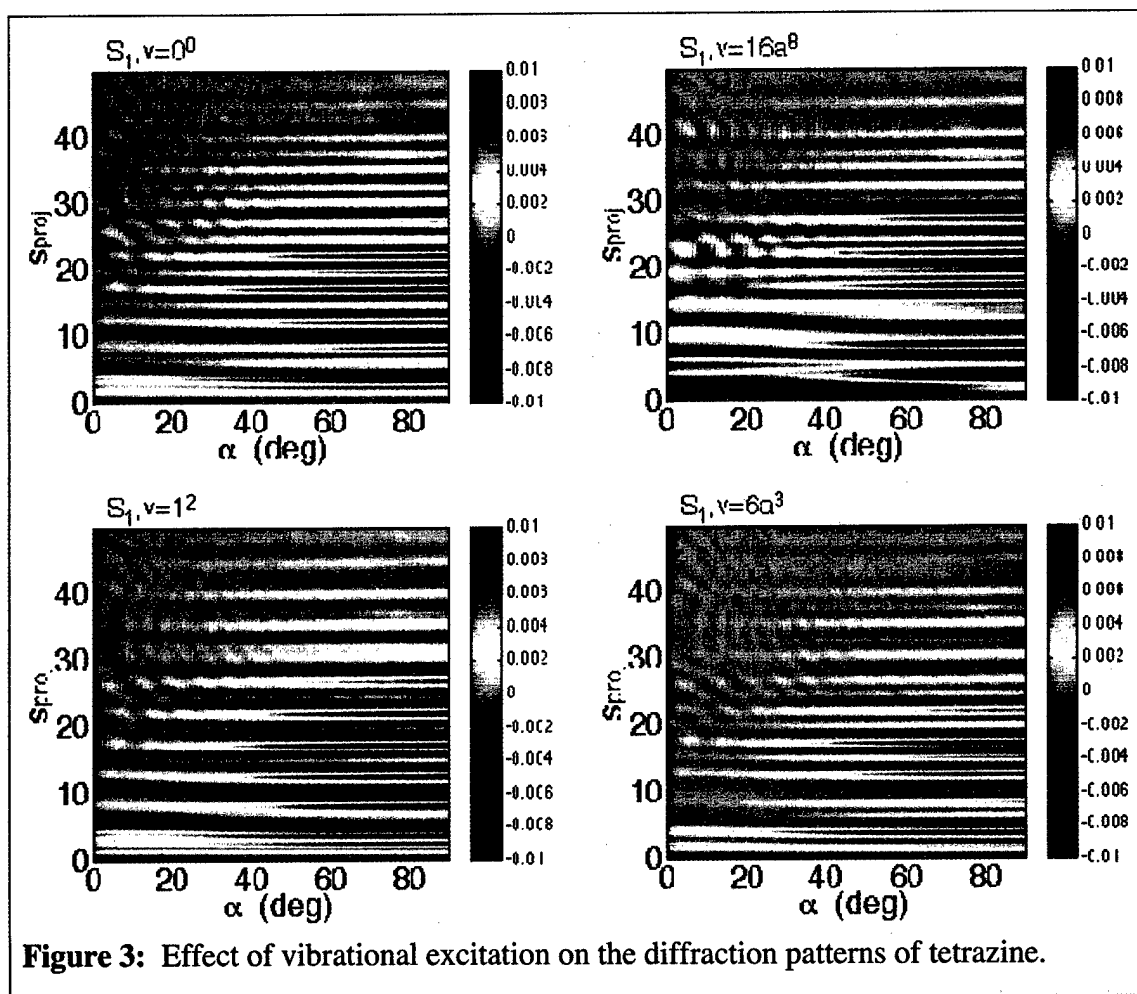


Figure 2: Diffraction from partially clamped and perpendicularly laser-aligned s-tetrazine molecules. Top panel, clamped at ($\theta = 90^\circ$, $\phi = 0^\circ$), with χ isotropic; Bottom panel, aligned in the y,z -plane by a circularly polarized laser pulse with 9.56×10^{12} W/cm².

The effect of the vibrational excitation is illustrated in figure 3. The diffraction patterns are for excitation to the vibrationless level, top left, and the vibrational states $16a^8$ (top right), 1^2

(bottom left), and $6a^3$ (bottom right), respectively. The color encodes the intensity of the ratio of the difference signal, divided by the signal from the un-excited molecules. It is clear that the vibrational excitation has a significant effect on the diffraction signatures of the molecules. Even a cursory inspection, looking at the regions of strong signal in the patterns, can reveal the identity of the vibrational mode.

The theoretical diffraction work forms the basis for two papers; one is submitted and received strong reviews, with only minor revisions suggested. The other is almost ready for submission.



Conclusions

The research performed during this funding period was very successful. We have met the stated objectives, and have discovered new frontiers. The Rydberg fingerprint spectroscopy may develop into a commercially viable and useful technique. The diffraction leads to the new science of tomography of vibrational motions in molecules. Both frontiers will be exciting to pursue in further explorations.

6. List of publications and technical reports

a) Published in peer-reviewed journals (2000 – 2003):

“A 9 eV superexcited state of 1,3-cyclohexadiene revealed by double resonance ionization photoelectron spectroscopy.” Wei Cheng, Conor L. Evans, Narayanan Kuthirummal, and Peter M. Weber; *Chem. Phys. Lett.* 349(5,6), 405-410 (2001).

“Ultrafast diffraction imaging of the electrocyclic ring-opening reaction of 1,3-cyclohexadiene,” Ray C. Dudek and P. M. Weber, *Journal of Physical Chemistry A*, **105**, 4167-4171 (2001) (A communication; our picture is on the cover!).

“Ultrafast dynamics in the 3-photon double resonance ionization of phenol via the S₂ electronic state,” Carolyn P. Schick and P. M. Weber; *J. Phys. Chem. A*, **105**, 3735-3740 (2001).

“Ultrafast dynamics in superexcited states of phenol,” Carolyn P. Schick and P. M. Weber; *J. Phys. Chem. A*, **105**, 3725-3734 (2001).

Submitted for publication

“Structure sensitive photoionization via Rydberg levels,” N. Kuthirummal and P. M. Weber.

“Diffraction signals of aligned molecules in the gas phase: tetrazine in intense laser fields,” S. Ryu, R. M. Stratt, and P. M. Weber.

“Rydberg states: sensitive probes of molecular structure,” N. Kuthirummal and P. M. Weber.

“Pump – Probe Electron Diffraction,” P. M. Weber, R. C. Dudek S. Ryu, and R. M. Stratt,” *Femtochemistry VI*.

“Probing Reaction Dynamics with Rydberg States: The Ring Opening Reaction of 1, 3-Cyclohexadiene”, N. Kuthirummal and P. M. Weber. *Femtochemistry VI*.

In preparation, nearing completion:

“Electron diffraction of molecules in specific quantum states: a theoretical study of vibronically excited s-tetrazine in intense laser fields,” Seol Ryu, Richard M. Stratt, Kyoung K. Baek, and Peter M. Weber.

b) Papers presented at meetings but not published in conference proceedings:

- 225th National Meeting of the American Chemical Society, New Orleans, LA, March 23-27, 2003: “Dynamics of Rydberg-excited 1,3-cyclohexadiene.” (Talk held by Narayanan Kuthirummal.)
- Workshop “Ultrafast science with x-rays and electrons,” Montreux, Switzerland, April 11, 2003: “Excited state structure, dynamics and wave functions by electron diffraction.”
- Ohio State University, Columbus, Ohio, January 31, 2003: “Pump-probe electron diffraction for probing excited states and chemical dynamics.”
- Ohio State University, Columbus, Ohio, January 29, 2003: “The foundations of electron diffraction.”
- Universität Karlsruhe, Karlsruhe, Germany, June 19, 2002: “Energy and structure: ultrafast dynamics in excited molecules.”
- 223rd National Meeting of the American Chemical Society, Orlando, FL, April 9, 2002: “Electron diffraction and photoelectron studies of the electrocyclic ring opening reaction of 1,3-cyclohexadiene.”
- University of Connecticut, Storrs, March 7, 2002: “Energy and structure: ultrafast dynamics in excited molecules.”
- 19th Austin Symposium on Molecular Structure, Austin, TX, March 4, 2002: “Time-Resolved Pump-Probe Electron Diffraction of 1,3-cyclohexadiene.”
- Universität Düsseldorf, Düsseldorf, Germany, January 17, 2002: “Spectroscopic and structural approaches to ultrafast molecular dynamics.”
- Universität Köln, Köln, Germany, January 14, 2002: “Energy and structure: ultrafast dynamics in excited molecules.”
- Gordon Research Conference ‘Photoions, Photoionization and Photodetachment’, July 2001: “Probing the electrocyclic ring opening reaction of 1,3-cyclohexadiene.” (‘Hot-topic’ talk).
- New England Regional Meeting of the American Chemical Society, June 25, 2001, Durham, New Hampshire: “The ring opening reaction of 1,3-cyclohexadiene: photoelectron and electron diffraction studies on femtosecond and picosecond time scales.” Narayanan Kuthirummal, Ray C. Dudek, Conor L. Evans, Wei Cheng, Job D. Cardoza, Jaimie Gosselin and Peter M. Weber. (Invited talk held by Narayanan Kuthirummal.)
- 9th Symposium on Gas Electron Diffraction, Blaubeuren, Germany, June 28, 2001: “Progress in real-time pump-probe electron diffraction.”
- Brookhaven National Laboratory, March 8, 2001: “Pump-probe diffraction experiments”
- University of Massachusetts, Amherst, February 8, 2001: “Ultrafast spectroscopy and diffraction.”
- Technische Universität, München, Germany, October 12, 2000: “Ultrafast dynamics in superexcited phenol.”
- Max-Born Institut, Berlin, Germany, October 10, 2000: “Pump-probe diffraction experiments.”
- UConn-Wesleyan-Yale Chemical Physics Seminar, October 3, 2000: “Ultrafast dynamics in superexcited phenol.”
- North Eastern Regional Meeting of the ACS, June 20, 2000; “Ultrafast dynamics in superexcited states of phenol.”
- 55th Ohio State University International Symposium on Molecular Spectroscopy, June 16 2000: “Studying the dynamics of the ring opening reaction of 1,3-cyclohexadiene.” (talk held by Ray Dudek)

7. Scientific Personnel

Peter M. Weber, principal investigator.

Narayanan Kuthirummal; post-doc.

Wei Cheng; graduate student (worked on this project, supported by other sources)

Job Cardoza; graduate student (worked on this project, supported by other sources)

Ray Dudek Degree: May 2001, Ph.D.: "Examining the ring-opening reaction of 1,3-cyclohexadiene using pump-probe electron diffraction."

Carolyn Schick, Degree: May 2000: "Femtosecond time resolved photoelectron spectroscopy of phenol."

8. Report of Inventions, and technology transfer:

"Methods and apparatus for the characterization and analysis of the shape of molecules and molecular clusters, and for the separation of desired isomers, based on Rydberg states." Patent application is pending.

Technology transfer to national laboratories

Over the last decade, we have pioneered the technology and theory of pump-probe structure determination using electron diffraction. As part of this work we have explored the generation of ultrashort electron pulses, applied them to model systems of chemical dynamics, and developed the theoretical framework of diffraction from excited states. Given this pioneering work, it is particularly rewarding to see that large national laboratories are starting to take note, and to design ultrafast electron diffraction facilities that are partially based on our work. Two national facilities, Brookhaven National Laboratory and the Stanford Linear Accelerator, have expressed interest in collaborating with us in the development of national user facilities to do time-resolved electron diffraction. Applications in a wide variety of fields, such as material science and biophysics, are foreseen, in addition to the continuation of the time-resolved dynamic studies. While both those facilities still await the requisite large scale funding, it is encouraging to note the level of activity that our work has stimulated.