CONF-8603121--1

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

MASTER

TITLE THE VIBRATIONAL SOLITON: AN EXPERIMENTAL OVERVIEW

LA-UR--86-1173

DE86 010167

AUTHOR(S) Irving J. Bigio

SUBMITTED TO Proceedings of the Special Sanibel Symposium
St. Augustine, Florida
March 8, 1986

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution or to allow others to do so for U.S. Government purposes.

The Los Alamos National Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

Los AlamosLos Alamos National Laboratory
Los Alamos, New Mexico 87545

THE VIBRATIONAL SOLITON: AN EXPERIMENTAL OVERVIEW

Irving J. Bigio

Los Alamos National Laboratory
Los Alamos, NM 87545
USA

ABSTRACT

To date the most convincing evidence of vibrational solitons in biopolymers has been found in two very disparate systems: Davydov-like excitations in hydrogen-bonded linear chains (acetanilide and N-methylacetamide) which are not biopolymers but plausible structural paradigms for biopolymers, and longitudinal acoustic modes of possibly nonlinear character in biologically viable DNA.

INTRODUCTION

The first biophysical theory to address the possibility of collective phenomena in biological systems was developed by H. Frohlich (Frohlich, 1968). In this generic theory a collection of oscillators interact nonlinearly as they exchange quanta with a heat bath. When pumped metabolically, a coherent state of the oscillators evolves that is reminiscent of a Bose-Einstein condensation. Later in 1973, Davydov and coworkers (Davydov, 1973) more specifically proposed that energy might be transported efficiently in alpha-helical protein molecules by means of a vibrational soliton. The excitation that they suggested invokes the coupling, through a nonlinear interaction, of amide-I vibrations (mainly C=O stretch) of the peptide groups with low-frequency phonons along the alpha-helix chain (mainly involving stretch of the hydrogen bonds between peptide groups). More recently Scott (Scott, 1982) extended the theory to the continuous limit (the excitation is distributed over a large number of peptide groups) resulting in the nonlinear Schrodinger equation for which the soliton is a traveling-wave solution. To date, to our knowledge, no definitive evidence of Davydov solitons in alpha-helix molecules has been published.

However, Scott (in collaboration with Careri and coworkers) has also done a similar analysis (Careri, 1983, 1984) for acetanilide (ACN), which is a linear hydrogen-bonded polypeptide, in order to explain the anomalous spectral feature which appears at low temperatures

at 1650 cm^{-1} . In this case the amide-I vibrations couple with an out-of-plane motion of the hydrogen-bonding proton, producing a new resonance reduced in energy by about 15 cm^{-1} from the fundamental at 1665 cm^{-1} . The self-trapped state is presumed to be stationary, and numerical modeling (Eilbeck, 1984) shows it to be quite localized. Figure 1a shows a simplified schematic of the molecular structure of ACN. Since many amides form hydrogen-bonded linear chains, structures like that of N-methylacetamide (NMA) pictured in Figure 1b would be expected to exhibit the same interaction.

More recently Scott has written a different nonlinear-dynamics theory (Scott, 1985) to describe the experimental results of Edwards et al. (Edwards, 1984, 1985) in which microwave resonances in DNA were demonstrated for the first time.

TECHNIQUES

Among the various laser and optical techniques, Raman and infrared spectroscopies are certainly the most common. Brillouin spectroscopy, IR-laser stimulation, nonlinear spectroscopies and hybrid techniques can also be employed.

Raman spectroscopy can address a large variety of transition symmetries since (in biopolymers) most dipole-allowed transitions are also Raman active. There is also the advantage of using visible wavelengths in a scattering mode to study infrared transitions, whereas IR-absorption spectroscopy (which works directly at the infrared wavelengths) often suffers from the media being opaque at those frequencies, and from other sample-presentation problems. On the other hand, infrared spectroscopy is generally much more sensitive than Raman for those transitions which are weak.

Brillouin spectroscopy employs difficult techniques that invoke multi-pass Fabry-Perot interferometers (Lindsay, 1984), but phonons and other excitations can be observed in the frequency range of $<50\text{ MHz}$ to 50 GHz which is generally not available to other techniques (except, under certain circumstances, for direct microwave resonance absorption).

Nonlinear spectroscopies, especially coherent anti-Stokes Raman spectroscopy (CARS), can also be useful, particularly with troublesome highly fluorescent samples. When picosecond lasers are used for CARS, transition lifetimes can be measured with resolutions to less than 10^{-12} s .

Infrared lasers can be built which can often be tuned to the vibrational transition of interest. Then an interesting hybrid technique is to observe the optical phonon region with Raman spectroscopy while stimulating a

specific vibrational transition with an infrared laser. This would be of interest, for example, if it were suspected that the vibration couples with a phonon via a nonlinear interaction. Such a scheme is represented schematically in Figure 2.

Most recently microwave spectroscopy has proven to be a useful technique for the frequency range of 100 MHz to ~40 GHz. Appropriate sample preparation and presentation are essential for success, and Edwards et al. (Edwards, 1985) have succeeded in using this method to study resonances in DNA which have generated much interest.

EXPERIMENTAL RESULTS

Reports of unusual Raman spectroscopic features in growth-synchronized cultures of metabolically active bacteria (Webb, 1980) have been difficult to duplicate. Other authors (Layne, 1995, and references therein) using different experimental techniques have reported that experimental artifacts and transient bursts of fluorescence in these cultures may be responsible for the previously reported spectra.

At this time, the most plausible experimental evidence for solitons in biopolymers is the Raman and IR spectroscopic data on ACN. While Careri and coworkers (Careri, 1973, 1983) have considered and discarded structural changes, phase transitions, etc. or Davydov splitting as possible explanations for the temperature dependence of the 1650 cm^{-1} line, Johnston and Swanson (Johnston, 1985) have suggested a Fermi resonance between the amide-I fundamental and a combination mode (the sum of the amide-II at $\sim 1550\text{ cm}^{-1}$ and an optical phonon at $\sim 100\text{ cm}^{-1}$). In their scheme the temperature dependences of the frequencies of the components of the combination mode are such that the Fermi coupling becomes stronger at lower temperatures, thus explaining the temperature variation of the 1650 cm^{-1} line intensity. Their publication also shows some isotopic-substitution data which is claimed to be confirmatory of the Fermi resonance explanation.

However, careful examination of the isotopic data and the addition of more recent data (overtone spectra) reopen the question to examination. The relative considerations are given below.

- (1) Both the IR spectra (Careri, 1983) and the Raman spectra (Johnston, 1985) show that the 1650 cm^{-1} line becomes more intense than the 1665 cm^{-1} line for temperatures below $\sim 100\text{ K}$. Since there are no other appropriate lines for intensity to be "borrowed" from, this indicates, in a Fermi interaction, a crossing of the original frequencies. Thus it is straightforward

to determine the sign of the anharmonic defect of the combination mode and to estimate its magnitude. The result is that for both the ^{12}C and the ^{13}C data to fit a Fermi resonance explanation, the anharmonicities for the two isotopes would have to be opposite in sign and greatly different in magnitude. There is no physical reason for the sign of the anharmonicity to change or for its magnitude to change significantly under isotopic substitution.

(2) Johnston and Swanson also mention an expected frequency shift of 30 cm^{-1} for the amide-I mode under ^{13}C substitution. However, a simple reduced-mass estimate gives a shift of 37 cm^{-1} . Figure 3 shows the ^{13}C data on an expanded scale for the amide-I region. The new location for the amide-I is down-shifted by the expected 37 cm^{-1} to $\sim 1627\text{ cm}^{-1}$, and it should be noted that in the cold spectrum there is also a smaller feature at $\sim 1613\text{ cm}^{-1}$, which is just 37 cm^{-1} down from the 1650 cm^{-1} line of the ^{12}C data. Since this line finds itself in the midst of strong features assigned to the benzene ring, it is to be expected that interference from these resonances would dampen the nonlinear interaction thus reducing the intensity of the "soliton" line.

(3) Under ^{15}N substitution or deuteration of the peptide group the effects are precisely as predicted in Scott's theory, but they do not disagree with a Fermi resonance interruption.

(4) The hallmark of a theory is a predictive capability. Scott and coworkers (Scott, 1986) have recently demonstrated that the self-trapped-state theory can predict the frequencies of the overtones of the vibrational soliton in ACN with reasonable accuracy. Here they derive the anharmonicity from the self-trapped state equations and use it to directly calculate the overtone frequencies. Experimentally in each case a temperature-dependent feature was found (with IR-absorption spectroscopy, at a frequency quite close to that of the predicted overtone. While there are numerous other temperature-dependent spectral features at various wavelengths, the requirements for positive identification of the identified features were several and quite rigorous.

As discussed earlier, NMA (and other hydrogen-bonded polypeptides) would be expected to exhibit nonlinear-dynamical effects similar to that in ACN. In an attempt to verify this, in collaboration with O. Faurskov Nielsen we have looked at the Raman spectrum of NMA at a few temperatures (Bigio et al., 1986). (NMA is a liquid at room

temperature and presents experimental problems of its own). Very preliminary data are shown in Figure 4. Here again there is a feature which appears only at reduced temperatures, in this case at about 1601 cm^{-1} (for 100 K) which is approximately 20 cm^{-1} below the amide-I line at 1621 cm^{-1} . The 20 cm^{-1} frequency separation is approximately what would be expected for a self-trapped state. Obviously more work is required on NMA to confirm the identification. This work is in progress (including the hybrid technique depicted in Fig. 2) and it is hoped that further results will be published in the near future.

Edwards, Davis and coworkers have recently demonstrated (Edwards, 1984, 1985) the existence of surprisingly narrow resonances in the microwave-absorption spectrum of DNA. The DNA was prepared so that every molecule in the sample was of the same length and sequence (from cloned plasmids with site-specific cuts). The resonances correspond to longitudinal acoustic modes of the molecules, but the frequencies measured lead to some potential confusion about the sound velocity. As mentioned above, Scott has offered a theory which incorporates nonlinearity (soliton-like character) in the molecular dynamics to explain the results (Scott, 1985). Both experiment and theory are currently benefitting from continued work and further refinement.

CONCLUSIONS

The best evidence to date for solitons in biopolymers has been found in molecular structures which are not really biological in nature but which are reasonable structural paradigms that can be studied rigorously. However, microwave techniques have been used with plasmid DNA and have resulted in data which may also have an exciting interpretation based on a soliton analysis (albeit different from the Davydov soliton). In general this field will benefit from enhanced interactions between theoreticians and experimentalists.

ACKNOWLEDGMENTS

This work was supported in part by the U.S. Naval Air Systems Command, the U.S. Department of Energy, and the Danish Natural Science Research Council. The author would especially like to thank the Danish Research Council for travel funds for collaboration with Prof. O. Faurskov Nielsen at the H.C. Orsted Institute of the University of Copenhagen.

REFERENCES

- Bigio, I.J., Nielsen, O.F. and Johnston, C.T., Proc. Hayashibara Forum on Computer Analysis for Life Science, Ohmsha Press, (in press, 1986).
- Careri, G., in: Cooperative Phenomena, eds. H. Haken and M. Wagner, p. 391 (Springer Verlag, 1973).
- Careri, G., Scott, A.C., et al., Phys. Rev. Lett. 51, p. 304 (1983).
- Careri, G., Scott, A.C. et al., Phys. Rev. B 30, p. 4689 (1984).
- Davydov, A.S. and Kislukha, N.I., Phys. Stat. Sol. (b), 59, p. 465 (1973).
- Davydov, A.S., J. Theor. Biol. 38, p. 559 (1973).
- Edwards, G.S., Davis, C.C., Saffer, J.D. and Swicord, M.L., Phys. Rev. Lett. 53, p. 1284 (1984).
- Edwards, G.S., Davis, C.C., Saffer, J.D. and Swicord, M.L., Biophysical Journal 47, p.799 (1985).
- Eilbeck, J.C., Lomdahl, P.S., and Scott, A.C., Phys. Rev. B 30, p. 4703 (1984).
- Frohlich, H., Int. J. Quantum Chem. 2, p.641 (1968).
- Johnston, C.T. and Swanson, B.I., Chem. Phys. Lett. 114, p. 547 (1985).
- Lindsay, S.M., Powell, J.W., and Rupprecht, A., Phys. Rev. Lett. 53, p. 1853 (1984).
- Scott, A.C., Physica Scripta 25, p. 651 (1982).
- Scott, A.C., Physica Scripta 32, p.617 (1985).
- Scott, A.C., Gratton, E., Shyamsunder, E. and Careri, G., (in press, 1986).
- Webb, S.J., Phys. Rep. 60, P.201 (1980).

Fig. 1a. Simplified structure of ACN

Fig. 1b. Simplified structure of NMA.

Fig. 2. A hybrid technique to study nonlinear dynamical interactions.

Fig. 3. Raman spectra of ^{13}C -substituted ACN.

Fig. 4 . Raman spectra of polycrystalline NMA at three temperatures.