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Two-dimensional and Third-order Nonlinear Laser Spectroscopy of Fused Heterocyclic Derivatives

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Abstract: *In optical research, the birth of laser has brought unprecedented development to the field of optics. This technology has been fully developed and applied when lasers have been developed and studied for a long time in the field of traditional spectroscopy. In addition, a lot of very important information can be received that cannot be obtained by these classical methods. The purpose of this paper is to study the two-dimensional third-order nonlinear laser spectroscopy of fused heterocyclic derivatives. A new method for third-order nonlinear laser spectroscopy, and in order to judge the accuracy of the method, the cascaded equation of motion method is used for comparison. The experimental results show that the time non-local quantum master equation is a relatively accurate method for solving the time evolution of the density matrix, so the matching method can obtain accurate two-dimensional third-order spectrum when solving the spectrum.*

Keywords: *Condensed Heteroderivatives; Nonlinear Optical Properties; Temporal Nonlocal Methods; Electron Spectroscopy*

1. Introduction

As humans explore the physical world, scientists are using more and more detection techniques. Initially, people observed macroscopic natural phenomena with the naked eye and summarized the laws of nature [1-2]. Humans then use magnifying glasses and microscopes to observe some microscopic objects. With the in-depth exploration of the microscopic world, we found that many detection methods, including electron microscopy, can observe the natural phenomenon of low or low dynamic energy transfer. Based on this limitation, many spectroscopic detection methods can indirectly detect the information of the molecular structure inside the measured substance, such as intermolecular binding force, dipole distribution, etc. [3-4].

The structures and kinetic processes of matter can be studied directly through their interaction with electric fields. Valuable detection tools such as nuclear magnetic resonance, microwave, infrared, ultraviolet, and X-ray spectroscopy have not yet been mastered [5-6]. There is fundamental interest in spectroscopic techniques for many different reasons. Spectrometers use radiation fields as a convenient means of detecting material systems. Optical engineers are interested in the electric field itself or the specific properties of new optical materials. Barriers to jargon are caused by differences in perspective and motivation. The main obstacle facing researchers in this field is the need to update many experimental methods [7-8]. Secondly, some related professional terms need to be updated uniformly to avoid language barriers in academic communication. Every new tip or slight change in laboratory equipment requires a name, making it nearly impossible to differentiate the information content of the various methods. Furthermore, the introduction of a common language hinders effective communication between different disciplines. This often results in parallel or unnecessary duplication of work and progress.

In this paper, on the basis of consulting a large number of relevant references, combining the importance of fused heterocyclic derivatives, nonlinear spectroscopy and nonlinear optical processes, a new method for simulating two-dimensional third-order nonlinear laser spectroscopy is proposed. The joint equation of motion method is compared to judge the accuracy of the method.

2. Two-dimensional and Third-order Nonlinear Laser Spectroscopy of Fused Heterocyclic Derivatives

2.1 The Importance of Fused Heterocyclic Derivatives

With the rapid development of modern organic chemistry and medicinal chemistry, the application of heterocyclic skeletons has become more and more extensive. Especially for small-molecule derivatives of drugs, the heterocyclic skeleton is in an irreplaceable position and is considered to be the "predominant structure" that must be studied first. Heterocyclic derivatives can be divided into single heterocyclic derivatives and fused heterocyclic derivatives [9-10]. A class of widely used substances, condensed heterocyclic skeleton, exists in many natural products and synthetic derivatives, has a wide range of biological activities, and is its basic structure.

At present, the derivatives of fused heterocycles have been widely used as medicines and fragrances, as well as intermediates of organic complexes. At the same time, many chemical coatings with new structures are also designed with fused heterocyclic framework as the main structure. Since the heterocyclic diffractoid plays the main function in the whole life system, the nitrogen-containing heterocyclic derivative is also the main branch of the heterocyclic diffractoid. From the development of penicillin drugs to the current fourth-generation reactor cephalosporins, medicinal chemistry is divided into antagonists of tumor pyrimidines, oral analgesics, barbiturates and sleeping pills, as well as antihypertensive drug reserpine. Diffraction bodies in the field of new drug research. In addition, fused heterocyclic diffractometers are also common in pesticides. It is believed that new pesticides with more structures will appear in the future development. In terms of derivative structure, heterocyclic derivative is a special kind of fused heterocyclic derivative. The main organophosphorus pesticides were phased out due to their high toxicity and replaced by new and effective fused heterocyclic pesticides.

Although fused heterocyclic derivatives are widely used in many industries, the synthesis of unique tricyclic frameworks remains a challenge, and the broad potential biological activities of fused tricyclic derivatives have not been fully investigated [11-12]. Therefore, it is promising to develop a widely applicable method for the synthesis of simple and fast fused heterocyclic molecules.

2.2 Nonlinear Spectroscopy

In order to study some content of nonlinear spectroscopy, we first briefly introduce some theoretical knowledge used in nonlinear optics in advanced quantum mechanics.

2.2.1 Hilbert Spaces

(1) Pure state and mixed state

All states of a quantum system discussed in quantum mechanics are represented by vectors in Hilbert space. This state is called pure state. If $\left|\psi_1\right\rangle$ and $\left|\psi_2\right\rangle$ are two pure states, another state $\left|\psi\right\rangle$ can be obtained by the superposition principle:

$$\left|\psi\right\rangle = \left|\psi_1\right\rangle C_1 + \left|\psi_2\right\rangle C_2 \quad (1)$$

Such a state is also called pure state.

However, in many cases, because the factors of statistical physics or the factors of quantum mechanics itself cannot be described by a state vector, the system at this time is not in a certain state, and may be in $\left|\psi_1\right\rangle, \left|\psi_2\right\rangle$,...... etc., and there are equal probabilities of P1, P2, .. Etc. between them. For such a state, we cannot use a state vector to describe the situation, which is called a mixed state.

(2) Reduced density matrix

In quantum mechanics, in order to explain the quantum state of a system and its change with time, the previous way usually assumes that the system is separated from the whole external environment, or completely separated. But this way is ultimately a way. Usually a subsystem of a larger system. So, for a fairly large complex system, how to find the average of subsystems associated with only a part of the system, if understood according to quantum mechanics, this is a system of degrees of freedom, and if this measurement correlates with the observed the degrees of freedom are correlated and are called incomplete measurements. Similarly, for a fairly complex system, if only the mechanical dimensions of the subsystem are seen, it is also an incomplete measurement. In this case, a low-density array is introduced to describe the quantum state of the subsystem.

2.2.2 Liuweier Space

Liouville space and Hilbert space are two corresponding spaces. The motion states of some microscopic systems can be described in the form of density matrices in Liouville space, which correspond to the representation of wave functions in Hilbert space. However, there are differences between the two. In Hilbert space, the various quantum states of an impure system have clear probability distributions. These cannot be described by a single wave function, but only by a density table. The canonical description, and thus the representation of the wave function, only applies to pure state systems. Based on the time-dependent *schrödinger* equation, Lee-Heller established the wave packet dynamics theory of absorption and scattering processes in Hilbert space. Inspired by Lee-Heller theory, time-varying spectrum theory was established and developed in Liouville combined with condensed phase spectroscopy experiments.

2.2.3 Nonlinear Influence Function

Maxwell's equations know to some extent the polarization intensity of light. It provides a very effective method for solving some problems in the field of radiation, while also playing an effective role in spectral measurements in the time and frequency fields. Calculating the polarization intensity of light is a major task in spectroscopic theoretical measurements. Observational analysis shows that the light response function must be solved to calculate the polarization intensity of the light.

2.3 Nonlinear Optical Process

(1) Second-order nonlinear optical process

The second-order nonlinear optical phenomenon can be regarded as the phenomenon produced by the interaction of three light waves in a nonlinear medium. Like other full-order nonlinear optics, second-order nonlinear optics can only be created on non-center-inversion symmetric media. Second-order nonlinear optical effects include frequency doubling (SHG), cumulative frequency (SFG), difference frequency (DFG), optical parametric amplification (OPA), and optical parametric oscillation (OPO).

The frequency doubling process is the most basic second-order nonlinear optical process, in which the photons of two frequencies ω are "coupled" into an optical component with a frequency of 20 by the interaction of incident photons and constitutive nonlinear materials. Therefore, the SHG process is generally used to convert the output power of visible-band infrared lasers. In the fields of biotechnology and medicine, SHG is mainly used in high-resolution light sensing microscopy. By using femtosecond laser irradiation on non-centrosymmetric biomaterials, such as collagen, microtubule structures, and tissues such as myosin, SHG information can be easily separated by applying appropriate filters or filtering the incident light. SHG microscopes offer considerable axial and lateral resolution, comparable to bifocal microscopes, without the need for apertures.

The sum-frequency process means that two photons with incident frequencies ω1 and ω2 combine to form one photon. SHG can be considered as a special case of SFG. The cumulative frequency is especially used when one of the two input frequencies is in the visible range of the spectrum and the other is in the infrared region. This enables in situ vibrational spectroscopy to be performed at the interface using a tuned infrared laser.

In the difference frequency, the generated photon frequency ω refers to the difference between the two frequencies of the incident photons ω1 and ω2. When the two reflected waves interact in the constitutive nonlinear lattice, the reflected wave with incident frequency ω2 can be amplified in the process of generating the frequency difference, that is, in the process of optical parameter expansion. This can be done by introducing two kinds of lasers to adjust different frequencies and amplify the adjusted lasers. Assuming that the optical measurement parameter amplification process occurs in the optical resonator, and the gain of the optical measurement parameter amplification is equal to the loss of the optical resonator, the coherent optical oscillation currently generated is called the optical measurement parameter oscillation. The wavelength of the optical parametric oscillator is determined according to the frequency of the current incident light.

(2) Third-order nonlinear optical process

The third-order nonlinear optical effect can be considered as the result of the interaction of four optical fields on the nonlinear medium, and the third-order nonlinear effect is generally weaker than the second-order nonlinear effect. Since this is the result of the interaction of the four electric fields, there are more interaction processes than side effects, except for effects similar to full frequency and difference frequency. According to the bipolar method, in general, only the materials with the center inversion symmetry of the broken line can produce the second-order nonlinear optical effect, but for the third-order nonlinear optical effect, for materials with different structures, the third-order nonlinear optical effect can be produced. Thus, basic third-order nonlinear visual effects are possible in all media. Typical third-order nonlinear optical effects include three-frequency (THG), two-photon absorption (TPA), two-photon fluorescence (TPF), four-wave mixing (FWM), Raman excited scattering (SRS), and Stokes.

Under the excitation of high-intensity laser, an atom or molecule needs to absorb two photons at the same time, and the sum of the total energy of the two photons is equivalent to the energy difference on the energy level of the medium. This is called simultaneous absorption of two photons. The process of absorbing the two photons can form the fluorescence of the two photons. When the particle absorbs two photons at the same time, it relaxes in an excited state. When the particle reaches the ground state, it emits a photon with a shorter wavelength than the original incident light, which is called two-photon fluorescence.

3. Experiment

3.1 The Matching Method of the Equation of Motion to Simulate the Spectrum

There are two architecturally different ways to calculate nonlinear polarization P, nonlinear spectroscopy has standard perturbation methods, that is, nonlinear polarization can be expressed as a response function.

Since the nonlinear electronic spectrum is obtained by the four-wave mixing technique, the third-order polarization induced by the three pulses is in either direction of the pulse matching (rotation) when using the equation-of-motion matching method. However, this method is only suitable for weak fields and is negligible for pulse overlap. In photosynthesis, weak fields are required for laser fields, so this framework is very powerful in photosynthesis calculations. The external electric field is expressed as a dipole moment.

$$H_{\text{int}}(t)=-\sum_{\alpha=1}^{3}\left(\exp\left\{i\vec{k}_{\alpha}\vec{r}\right\}v_{\alpha}^{(+)}(t)+\exp\left\{-i\vec{k}_{\alpha}\vec{r}\right\}v_{\alpha}^{(-)}(t)\right) \quad (2)$$

$$v_{\alpha}^{(\pm)}=V\lambda_{\alpha}E_{\alpha}(t-t_{\alpha})\exp(\mp i\omega_{\alpha}t) \quad (3)$$

Where λ_{α}, k_{α}, ω_{α}, $E_{\alpha}(t)$ represents the intensity, wave vector, frequency and wave packet, respectively. V is the dipole momentum operator.

3.2 Numerical Simulation

The temporal nonlocal method of solving the density table includes non-Markov phenomena, but since the higher-order term of the diffusion term is omitted, is it compared with the exact solution when solving the density table, and then the nonlocal time method and the motion waterfall method are used, see if the dynamics of the two evolve significantly over time.

Using the non-local time method and the waterfall equation of motion, we simply model the dynamic evolution of the energy transfer in the FMO complex and see the difference between the two methods, the matrix of the FMO Hamiltonian is:

$$H_{fmo}=\begin{pmatrix} 200 & -87.4 & 5.4 & -5.8 & 6.6 & 13.6 & -9.8 \\ -87.4 & 320 & 30.7 & 8.1 & 0.6 & 11.7 & 4.2 \\ 5.4 & 30.7 & 0 & -53.4 & -2.1 & -9.5 & 5.9 \\ -5.8 & 8.1 & -53.4 & 110 & -70.6 & -16.9 & -63.2 \\ 6.6 & 0.6 & -2.1 & -70.6 & 270 & 81 & -1.3 \\ 13.6 & 11.7 & -9.5 & -16.9 & 81 & 420 & 39.6 \\ -9.8 & 4.2 & 5.9 & -63.2 & -1.2 & 39.6 & 230 \end{pmatrix} \quad (4)$$

4. Discussion

The spectral density taken in this paper is $J(\omega)=\frac{2\lambda\omega\gamma}{\omega^2+\gamma^2}$, and the parameter values taken in it are $\lambda=34cm^{-1}$, $\gamma=52.07cm^{-1}$, so that the comparison results of the two methods can be obtained.

Table 1: Layout time evolution map of FMO complexes

	1	2	3	4	5	6	7
0	1.0	0	0	0	0	0	0
200	0.526	0.318	0.078	0.047	0.038	0.034	0.036
400	0.482	0.252	0.136	0.068	0.046	0.036	0.043
600	0.413	0.237	0.187	0.115	0.052	0.039	0.051
800	0.395	0.206	0.206	0.126	0.068	0.046	0.067
1000	0.3	0.164	0.224	0.159	0.074	0.051	0.073

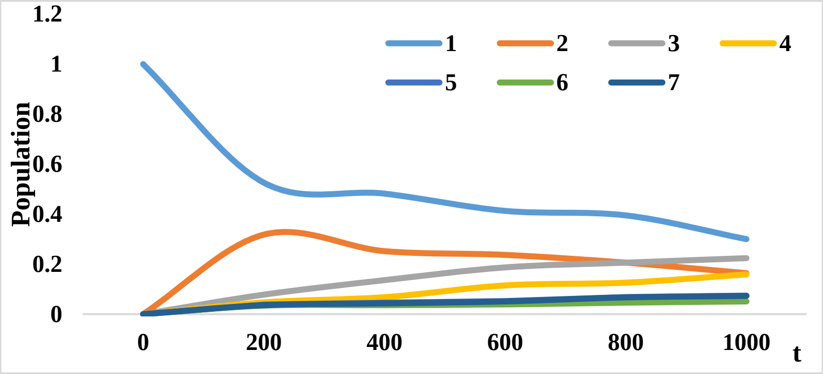

Figure 1: Initial state 1

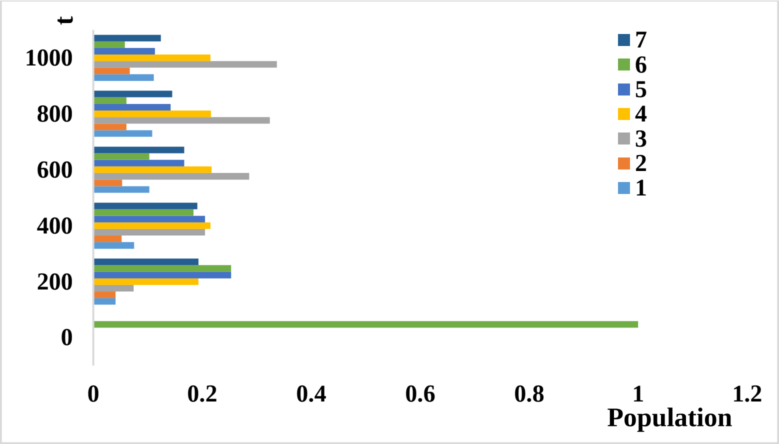

Figure 2: Initial state 2

Since the FMO has two energy transfer paths, there are two cases to consider when choosing the initial state. From the above figure, there is no obvious difference in the progress of the energy transfer between the two simulation methods, and the time delocalization method diffusion terms are truncated higher-order terms, but the value of these truncated higher-order terms is very small, which can be ignored, indicating that time nonlocality is a relatively accurate method.

5. Conclusion

Experimentally, the two-dimensional nonlinear spectral images obtained from the interaction of the laser field and matter can macroscopically display the dynamic process of microscopic interactions and system evolution, which is a very complex experimental technique. Because the laser pulse delay and laser pulse intensity need to be precisely controlled to obtain two-dimensional nonlinear spectra in experiments, and two-dimensional electron spectroscopy plays a very important and practical role in determining atomic structural information.

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