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論文内容の要旨

TTF-CA is a typical mixed-stack charge transfer compound, which undergoes neutral (N) to ionic (I) phase transition by lowering the temperature or applying high pressure. This N-I phase transition is confirmed to be a first order one and induces various changes in TTF-CA on its structural, optical and magnetic properties. The low temperature I-phase is characterized by a lattice dimerization along the stacking direction, while the starting N-phase is monomeric and has no dimerization. Charge transfer (CT) absorption spectral shape in the I-phase has a two-headed structure in contrast to the single-peak one in the N-phase spectra. Electron spin resonance line shape indicate the creation of a constant spin density below transition temperature, while the dc conductivity data show the evidence of mobile charge carriers at the onset of the I-phase. Besides the temperature-induced or pressure-induced phase transitions, a photoinduced I-to-N phase transition (PIPT) has also been discovered by using femto-second spectroscopic techniques. It is found that a macroscopic neutral domain can be generated in the I-phase of TTF-CA by shining a strong laser light of about 0.6eV~2.2eV onto TTF-CA, even when the temperature is very low. Recent studies on this PIPT reveal that the N-phase generation efficiency quite sensitively depends on the way of the excitation. For the typical CT excitations, the PIPT has a noticeable threshold excitation intensity, below which the macroscopic neutral domain can not be generated. However, for the intramolecular excitations, the N-phase generation efficiency has no significant threshold excitation intensity. These behaviors reveal the highly nonlinear nature of PIPT.

We present a theoretical work to study this photoinduced I-to-N structural phase transition from a unified point of view. Using the adiabatic approximation and the mean-field theory, we investigates an extended Peierls-Hubbard model to clarify various features of TTF-CA, ranging from the ground state properties, the absorption spectral shape, to the nonlinear lattice relaxation of the CT exciton. Our model includes strong inter-molecular Coulomb interactions, which depend nonlinearly on the inter-molecular distance. A weak inter-chain interaction is also taken into account to describe the formation of the macroscopic neutral domain in the three-dimensional ionic phase. In the ground state, the quasi-I phase is just below the quasi-N one. Both these I- and N-phases are locally stable, and a low energy barrier separates them. In the I-phase, the lattice has 3% dimerization along the stack axis,

while the N one is monomeric and has no dimerization. Based on this mean-field picture, the N-I phase transition in TTF-CA is classified to be the first order.

To calculate the optical absorption spectrum, we have developed a classical Monte-Carlo theory to take the thermal lattice fluctuations into account. The exciton effect is also included by using the first order perturbation theory. The resultant spectrum illustrates the peculiar two-headed shape, which agrees with the experimental one. Thus we could well reproduce the position of these two peaks as well as the relative intensity between them.

By studying the nonlinear lattice relaxation processes of the CT exciton, we have clarified the adiabatic relaxation path, which starts from a Franck-Condon state and terminates up to the large neutral domain formation in the ionic phase. The ground state energy surface reveals that this neutral domain becomes stable only when its size is large. Moreover, the first excited state of the neutral domain is little above the Franck-Condon state, and these two states are separated by a high barrier. Therefore the lowest state of a single CT exciton can not relax down to the neutral domain straightly, but a large excess energy is necessary so that it can overcome the barrier. This theoretical result explains the origin of the threshold excitation intensity, below which the macroscopic neutral domain can not be generated by the photons resonated to the CT exciton. It has been also discovered that there exist various shallow minima on the energy surface of the ground state. These minima prevent the fast decay of the neutral domain, and let it have a fairly long lifetime. We also investigate the anti-phase ionic domain. This domain is above the neutral one, and a low barrier separates them. Thus, even if the anti-phase ionic domain is generated just after the photoexcitation, it will soon relax down to the neutral one. These findings are consistent to the recently obtained time-resolved experimental results. Furthermore, we illustrate the charge and the spin distributions of the neutral domain. Our results show that the ground state of the NIDW can carry a unit charge and spin, however, its first excited state can carry almost none of them. The radiative or nonradiative decay of the excited NIDW is found to be quite difficult, so that, the first excited states can have fairly long lifetime, if we restrict ourselves within the mean-field theory.

論文の審査結果の要旨

ＴＴＦとＣＡという２種類の有機分子を１対１の組成で混合した結晶をつくると、絶対零度ではＴＴＦからＣＡへ電子が移動し（ＴＴＦ）$^{+}$ と（ＣＡ）$^{+}$ とにイオン化した相が形成される。ところが腰原・十倉等の先駆的実験によれば、この物質にレーザー光を照射すると分子間で逆電荷移動が起き、（ＴＴＦ）^{0} と（ＣＡ）^{0} とからなる中性対が生れ、さらにこの対が１０００個の巨視的規模に自己増殖し中性相のドメインが生成する事が判明した。これは、光誘起構造相転移と呼ぶべき現象である。更に谷村の実験によれば、この中性相発生効率には励起光強度に明瞭な閾値が存在し、線形励起の範囲内では相転移は発生せず、数個の励起が非線形の協力現象を起こして始めて中性相が発現する事が判明した。しかし、この非線形性の起源に関しては明瞭な解答がなく、国内外の研究者間で大きな懸案となっていた。

怀平君はこれを理論的に解明するため、この物質の基底状態、光励起状態及びその格子緩和過程と励起ドメイン生成過程を一貫した方法で理論的に考察した。この理論はＴＴＦとＣＡの価電子のみを考慮し、この電子集団での電子の量子的運動、電子間長距離クーロン斥力および格子変位によるこの長距離クーロン斥力の変化をモデル化したものである。計算には断熱近似と平均場近似を適用している。又、励起状態には単純ＣＩ法を適用して計算した。この理論によって、この物質の熱的イオン性から中性相への相転移が一次相転移となる事や近赤外域での光吸収スペクトルの形状など、実験的に得られている特徴が良く再現される。

また、この理論によって一個の電荷移動励起と中性ドメインとが励起状態のポテンシャル面上で高いバリヤーによって相互に隔てられている事が立証された。つまり、吸収端のごく近傍のエネルギーで電荷移動励起が一個のみ励起されても、それだけでは中性ドメインへは到達出来ない事が立証された。吸収端よりも十分高いエネルギーを持つ光子を多光子の形で注入して始めて、協力現象が起きドメインの発生が可能になる事が結論された。これは、実験で観測されている閾値の起源を始めて明らかにしたものである。

以上、怀君の研究は、この研究分野の懸案となっていた問題に明瞭な解答を与えるものであり、提出された論文は、博士学位論文として十分な価値があると認められた。