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Excited-State Dynamics in Isolated 2,2'-Bithiophene

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Even though the S_1 state of isolated 2,2'-bithiophene lives less than 8 ns, the temporal profile for S_1 resonance-enhanced two-photon ionization is in the microsecond domain. The observed kinetics may be quantitatively understood if it is assumed that the initially prepared S_1 state decays sequentially through two different long-lived triplet states. This paper presents and analyzes the measured profiles.

Introduction

Experimental determination of the electronic structure and photophysical behavior of bithiophene (Figure 1) is important for a number of reasons. First, since it is an oligomer of polythiophene, bithiophene serves as a model system for evaluating theoretical models that are being developed to provide a microscopic understanding of charge transport and nonlinear optical response in the polymer.^{1,2} Second, since it may be viewed as a substituted polyene, studies of the electronic structure of bithiophene can contribute to our understanding of the effects of chemical perturbation on linear polyene electronic structure.³⁻⁵ Third, since bithiophene consists of two relatively rigid rings, there is only one conformational coordinate for unimolecular photochemistry: rotation about the interring bond which takes the rings from a *trans* to a *cis* relationship.⁶ It is thus an excellent model system for studying photochemical isomerization. The measurement of vibrationally resolved optical spectra for *cis* and *trans* bithiophene and the determination of the ground- and excited-state potentials for *cis-trans* interconversion are described in another paper.⁷

In that study we used fluorescence excitation techniques to measure spectra for bithiophene seeded into supersonic helium expansions and established that the decay time for the emission was substantially less than 10 ns. Thus, we were quite surprised to find that, although the excitation spectrum for 1+1 resonance-enhanced multiphoton ionization was identical to the fluorescence excitation spectrum, essentially all of the resonance enhancement came from a state whose kinetic behavior lies in the microsecond regime. This paper reports the dynamics associated with 1+1 resonance-enhanced multiphoton ionization and analyzes these data in terms of a model involving the sequential population of two long-lived states.

Experimental Section

Apparatus and Materials. Our apparatus for measuring resonance-enhanced multiphoton ionization spectra of jet-cooled molecules has been described in detail.⁸ For these experiments there were only two significant changes from the original setup: the Nd:YAG laser has been modified so that we now have the ability to pump the pulsed dye laser with either a donut-shaped beam spatial profile or a near-Gaussian beam spatial profile, and a Burleigh PWA4500 pulsed wavemeter which permits the direct measurement of the wavelength of the light produced by the dye laser has been added. The wavelength of the UV light produced by frequency doubling the dye laser output is now obtained by halving the wavelength measured by the wavemeter.

Bithiophene was purchased from Aldrich and used without further purification. The dye solution for the tunable laser was made with DCM purchased from either Exciton or Lambda Physik dissolved in HPLC grade methanol purchased from Fisher.

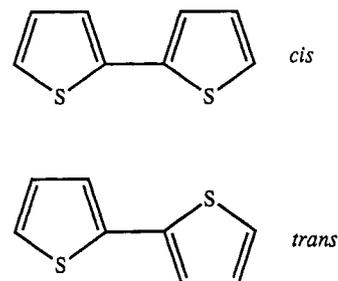


Figure 1. Chemical structures of *cis*- and *trans*-2,2'-bithiophene.

Procedures. In a typical experiment, a few crystals of bithiophene were placed in a 5 mm diameter Pyrex culture tube which was inserted into the stainless steel reservoir that serves as the source for our pulsed nozzle. After it was sealed, the reservoir was wrapped with heating tape, heated to *ca.* 70 °C, and pressurized with *ca.* 2 atm of helium gas. The pulsed valve and nozzle were also heated to *ca.* 70 °C.

Excitation spectra could be obtained from either a one-color experiment or a two-color experiment. In the one-color experiments, the frequency-doubled output of the dye laser was used both to excite the jet-cooled bithiophene and to ionize the excited molecules. For two-color experiments the dye laser intensity was attenuated to suppress the one-color ionization signal and a pulse of 193-nm photons from an excimer laser (Lambda Physik LPX1052) ionized the excited molecules. As before,⁸ the dye laser pulse was focused with a 10 cm focal length lens onto the intersection of the dye laser and molecular beams while the excimer laser pulse was not.

Pump-probe two-color experiments to determine the time dependence of the ion signal as a function of the delay between the dye laser and the excimer laser pulses followed the protocol that we previously applied to 1,3,5,7-octatetraene.⁸ For each data point on a given decay curve the delay between the tunable dye laser and excimer laser trigger pulses was manually set and read with the HP 54502A digital oscilloscope. The excimer laser trigger pulse was coincident with the opening of the 100 ns wide boxcar gate. We also tried a second method using a digital delay generator (EG&G Model 9650), which could be controlled by computer through an IEEE488 interface, to manage the timing of the experiment. Although this should have made it possible to collect significantly more data, we unfortunately found that our instrument could not reliably scan one delay with respect to other delays and, at several points in a time delay scan, the delay generator ceased to trigger the laser. Only data collected by the first method are presented and analyzed in this paper.

Experimental Results

The excitation profile for two-color 1+1 photoionization of 2,2'-bithiophene seeded in a supersonic helium expansion is shown in Figure 2. The spectrum in Figure 2 is indistinguishable from

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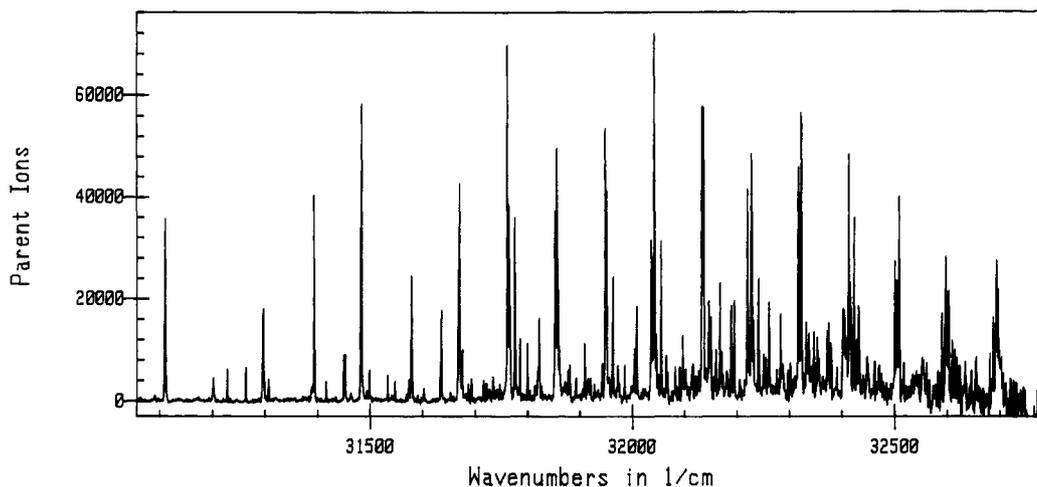


Figure 2. Resonance enhancement profile for 1 + 1 multiphoton ionization of bithiophene seeded in a supersonic helium expansion. This excitation profile is identical to the S_1 fluorescence excitation spectrum measured under the same conditions.

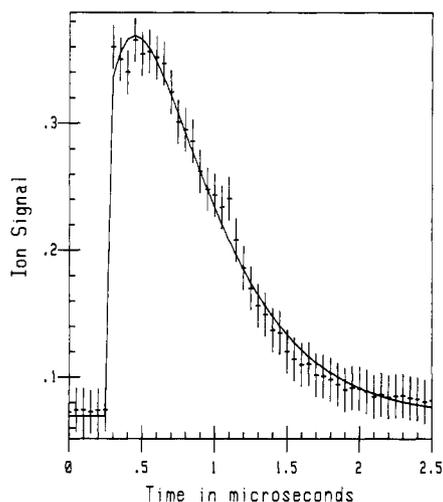


Figure 3. Kinetics of 1+1 two-color two-photon ionization of bithiophene seeded in a supersonic helium expansion. In this figure the number of parent ions generated by the probe pulse (ArF excimer laser) is plotted against the delay between the excitation (dye laser tuned to the 0-0 band of *trans*-bithiophene) and probe pulses. The smooth line drawn through the experimental points is the theoretical curve for sequential decay of S_1 through two triplet states.

the fluorescence excitation profiles that we have previously measured and analyzed,⁷ which establishes only that the resonance enhancement comes from excitation of the S_1 state. It does not follow that the transition to the continuum originates from this state; it can originate from any subsequently populated state that is within $h\nu$ of the ionization limit. We now turn to the dynamics of the resonance enhancement which clearly show that photoionization is *not* from the initially populated S_1 state.

In all, eight decay curves (a total of 437 data points) were selected for analysis: three for excitation at the 0-0 of the *trans* isomer (31 111 cm^{-1}), three for excitation at the 118- cm^{-1} band of the *trans* isomer (31 229 cm^{-1}), and two for excitation at the 0-0 of the *cis* isomer (31 203 cm^{-1}). All of the measured decay curves are very similar to the one shown in Figure 3.

The Kinetic Model

Our measurements of fluorescence excitation spectra of bithiophene seeded into a supersonic helium expansion⁷ clearly show that the lifetime of the excited singlet state is too short to be measured with our *ca.* 8-ns FWHM pulsed lasers. This fact together with the qualitative appearance of the plot of the relative number of parent ions produced versus time delay between the excitation and ionization pulses in the two-color 1+1 resonance-

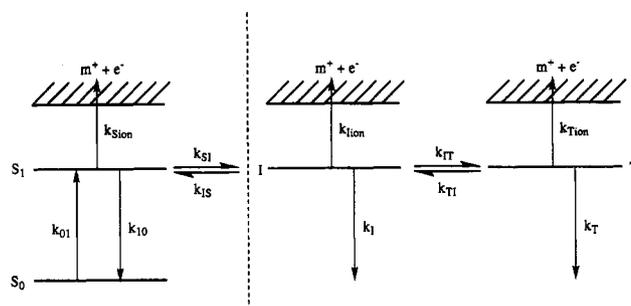


Figure 4. Kinetic scheme for the 1+1 two-color two-photon ionization of isolated bithiophene.

enhanced multiphoton ionization shown in Figure 3 does much to define the interpretative model. The fact that the signal rises with the excitation pulse profile but then evolves on a microsecond time scale means that the state responsible for the resonance enhancement is not the initially excited S_1 state. The fact that the time evolution is most certainly not a simple exponential means that more than one long-lived state is involved. We think that at least the final state must be an excited triplet state. This leads us to the kinetic scheme sketched in Figure 4.

The fluorescence excitation studies⁷ establish that all processes that affect the population of the excited singlet state S_1 (excitation rate constant $k_{01} = \sigma_{01}I_{\text{laser}}$, decay rate constant $k_{10} = \sigma_{01}I_{\text{laser}} + k_d$, and equilibrium with the intermediate level characterized by rate constants k_{S1} and k_{IS}) are fast on the nanosecond time scale. This means that direct ionization of S_1 (rate constant $k_{Sion} = \sigma_{Sion}I_{\text{laser}}$) can only contribute to the first few nanoseconds of the measured profile. Since there is no significant short time spike, only the processes to the right of the dotted line in Figure 3 are relevant. Thus, the data should be fit by a two-state model involving an initially populated intermediate state I connected to a triplet state T where the rate constants for photoionizing I and T by the excimer laser pulse are $k_{Iion} = \sigma_{Iion}I_{\text{laser}}$ and $k_{Tion} = \sigma_{Tion}I_{\text{laser}}$, respectively. That is, in this model the observed decay curves are just a superposition of the time-dependent fractional populations of the I and T states. The most general expression for such a superposition is

$$\text{Ions} = \exp(-\lambda_1 t) - A \exp(-\lambda_2 t) \quad (1)$$

where $\lambda_{1,2} = -1/2 \{ (k_1 + k_{IT} + k_{TI} + k_T) \pm [(k_1 + k_{IT} - k_{TI} - k_T)^2 + 4k_{IT}k_{TI}]^{1/2} \}$. The measured curves are well fit by eq 1 (see, for example, Figure 3): the parameters obtained by fitting eq 1 to the measured curves and the quality of fit are summarized in Table 1.

TABLE 1: Kinetic Parameters and Quality of Fit for Modeling the Time Evolution of the Resonance-Enhanced Two-Photon Photoionization of Bithiophene Seeded into a Supersonic Helium Expansion by the Expression $Ions = e^{-\lambda_1 t} - Ae^{-\lambda_2 t}$

resonance	λ_1 in (μs) ⁻¹	λ_2 in (μs) ⁻¹	A	RMS dev/ RMS value
<i>trans</i> isomer 0-0 (3 decay curves)	1.680	1.697	0.986	0.004
<i>trans</i> isomer 118 cm ⁻¹ (3 decay curves)	1.927	1.942	0.994	0.013
<i>cis</i> isomer 0-0 (1 decay curve)	1.908	1.927	0.987	0.005
all data (7 decay curves)	1.792	1.812	0.990	0.007

Full determination of this kinetic model would consist of obtaining values for the four rate constants plus the relative cross sections for photoionizing from the I and T states. While it is not possible to unambiguously extract five quantities from data that are fit with a three-parameter expression, the range of possibilities for these five parameters is surprisingly narrow. Two of the four rate constants are quite precisely determined by the measured data, as is the sum of the other two. Further, the relative photoionization cross sections are constrained, and for each allowable value of the relative amplitudes of the I and T state photoionization channel values, all four rate constants are fixed. This is discussed further in the next section.

Kinetic Parameters

Table I shows that when eq 1 is fit to the measured curves, the values of λ_1 and λ_2 are nearly equal. In numerical simulations we have found that with the constraint that k_{IT} is significant and that all rate constants are positive this can only be the case if either k_{TI} or k_{IT} is very close to zero. If k_{IT} is nearly zero, then there is no possibility for biexponential behavior, so it follows that $k_{TI} \approx 0$. Since k_{TI} is the rate of a reverse dephasing process, it is quite reasonable to expect it to be small. For $k_{TI} = 0$, $\lambda_1 = k_T$ and $\lambda_2 = k_I + k_{IT}$.

From the fact that the ion signal rises with the excitation laser pulse, it follows that there must be photoionization from the I state. This is also implied by the deviation of the A parameter in eq 1 from 1.0. If $\sigma_{Iion}/\sigma_{Tion} = \alpha$, then $A = 1 - \alpha(k_I + k_{IT} - k_T)/k_{IT}$. Equations 2-4 summarize the possibilities for α , k_I , k_{IT} , and k_T given the constraints that k_{IT} must be finite and that rate constants must be positive.

$$k_T \cong \lambda_1 \quad (2)$$

$$k_I + k_{IT} \cong \lambda_2 \quad (3)$$

$$\alpha \cong \frac{(1-A)(\lambda_2 - k_I)}{\lambda_2 - \lambda_1} \quad (4)$$

As is seen in Table 1, the best values for the parameters λ_1 , λ_2 , and A for the three different excitation conditions differ only

slightly. Using the λ_1 , λ_2 , and A values determined by simultaneously fitting all of the decay profiles (the last line in Table 1), we obtain

$$k_T = 1.79 (\mu\text{s})^{-1} \quad (5)$$

$$0 \leq k_I \leq 1.81 (\mu\text{s})^{-1} \quad (6)$$

$$0 < k_{IT} \leq 1.81 (\mu\text{s})^{-1} \quad (7)$$

$$0 < \alpha \leq 0.91 (\mu\text{s})^{-1} \quad (8)$$

While we see no alternative to the final state T being a triplet state, there is the possibility that the intermediate state I is the highly vibrationally excited ground state. There are two strong arguments against this assignment. First, if the intermediate state I were the vibrationally excited ground state, it would be hard to rationalize the fact that k_{IT} must be much larger than k_{TI} since density of states considerations would lead to the opposite prediction. Second, the deviation of the A parameter from 1.0 can only be understood if the cross section for photoionization from the I state is significant compared to the cross section for photoionization from the T state. Franck-Condon considerations lead to the prediction of negligible photoionization from the vibrationally excited ground state.

Conclusions

Two-photon photoionization of isolated 2,2'-bithiophene is significantly enhanced by resonance with the S_1 state, but the observed dynamics show clearly that the dominant channels for photoionization involve long-lived triplet states into which S_1 decays. To fit the observed temporal profiles, sequential decay of S_1 through two triplet states must be invoked. The data determine relatively narrow ranges for the rates associated with this sequential decay. In particular, the kinetic analysis establishes that the decay rate for the final triplet state is $1.79 (\mu\text{s})^{-1}$ (lifetime = 550 ns) and that both triplet states contribute to the photoionization.

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