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Resolution of different conformers of methoxy-trans-stilbenes via rotational coherence spectroscopy

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Abstract

The excitation spectra of 4-methoxy-*t*-stilbene (MoS) and 4-methoxy,4′-methyl-*t*-stilbene (MoMeS) both exhibit two electronic origin transitions, separated by 260–280 cm^{-1}. This suggests the presence of two structural forms, as predicted by semi-empirical quantum mechanical calculations. The two forms should be 'syn' and 'anti', where the methoxy group is coplanar with the mean plane of the aromatic molecule. Rotational coherence spectroscopy has identified the syn and anti rotamers of the two species, establishing in both cases that the syn form has the longer-wavelength absorption.

1. Introduction

The fluorescence excitation spectrum of 4-methoxy-*t*-stilbene (MoS) was recently reported by Siewert and Spangler (SS) [1], who assigned transitions at 30744 and 31023 cm^{-1} as two 0_0^0 bands (see Fig. 1 (upper)). They attributed the existence of two origins to the two planar conformers of the methoxy group, which derive their energy difference from syn and anti orientations with respect to the ethylene group. This geometry is supported by the following evidence. The parent molecule trans-stilbene has a planar structure, known from vibronic assignments [2], rotational coherence spectroscopy [3] and rotationally resolved studies [4]. Also, symmetry restrictions on the observation of out-of-plane ring modes remain in MoS, since they appear only as overtones [1]. Finally, semi-empirical calculations using the AM1 Hamiltonian predict similar energy minima for the syn and anti conformers (within 50 cm^{-1}) and a barrier of nearly 600 cm^{-1} for the perpendicular methoxy orientation.

The observed conformer energy difference for the excited state is significantly greater than the calculated difference for the ground state. SS attribute this to greater π-electron delocalization in S_1 which, in turn, allows stronger interaction between the ethylene, remote ring, and the substituent. Conversely, the large electronic origin shift (≈ 270 cm^{-1}) suggests that the electronic interaction between the methoxy group and the *t*-stilbene π-electron system differs significantly for the syn and anti orientations. Of these, the red-shifted origin (origin I, Fig. 1) probably belongs to the conformer that is the better electron donor. The reasoning is that the red shift is predominantly due to excited state stabilization due to greater π-electron delocalization. This effect should be greater for the stronger donor. A higher

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ν_{37} ring torsion frequency (which is sensitive to the C_e–phenyl bond order) for origin I supports this reasoning.

This issue was further addressed by SS through investigation of the derivative, 4-methoxy-4′-methyl-*t*-stilbene (MoMeS) which exhibits comparably spaced origins at 30517 and 30783 cm^{-1} (see Fig. 1 (lower)). Here, both conformers exhibit methyl torsional splitting at the 0_0^0 position, and in conjunction with other principal vibronic bands such as ν_{25}. Higher-energy members of the methyl torsional progression were also identified by SS. Earlier work by Yan and Spangler [5] established that a strong electron donor, such as an amino group, in the 4-position

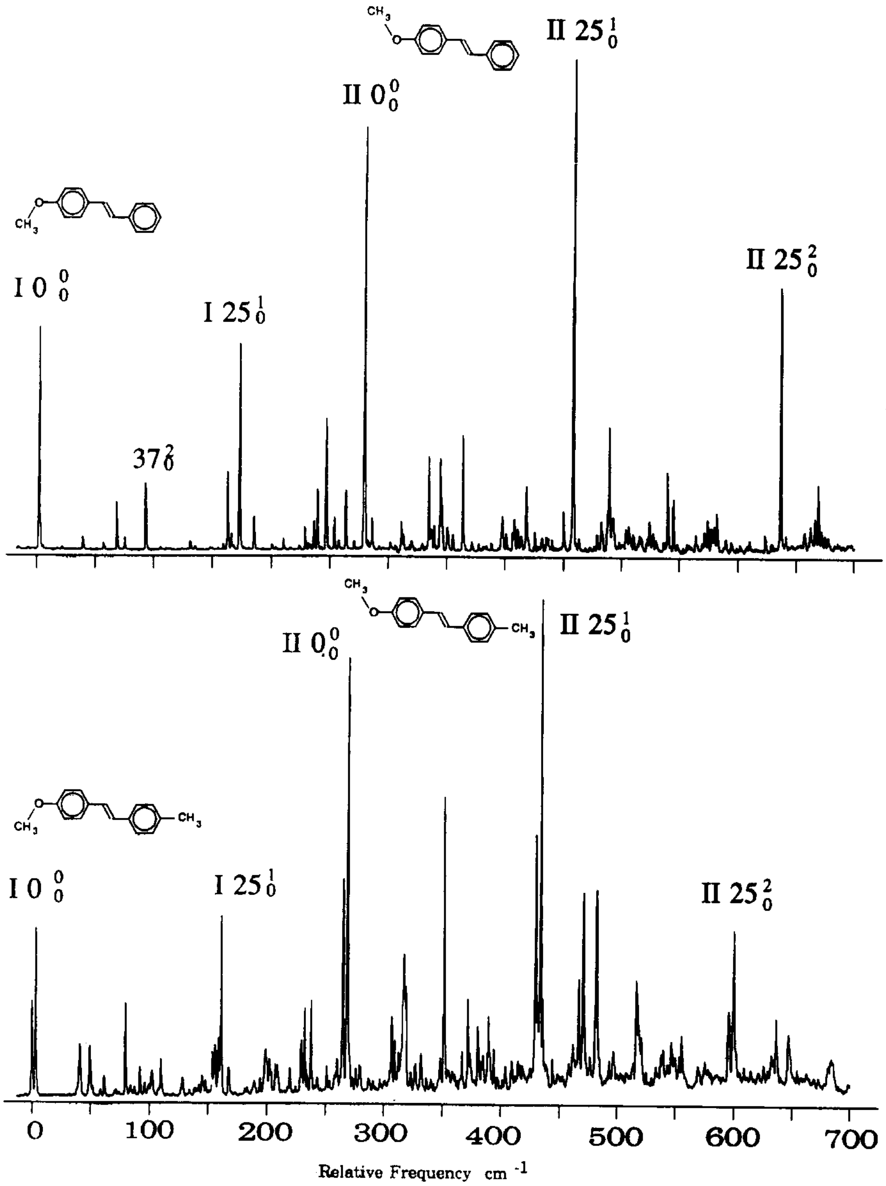

Fig. 1. Fluorescence excitation spectra for MoS (upper) and MoMeS (lower) obtained by Siewert and Spangler. The assigned structures for the two conformers in each case are now proven by the current work.

of 4′-methyl-*t*-stilbene lowers the methyl torsional barrier in S_1. The ≈ 100 cm^{-1} S_1 barriers measured for MoMeS are intermediate between those of 4-methyl-*t*-stilbene (150 cm^{-1}) and 4-amino-4′-methyl-*t*-stilbene (55 cm^{-1}). This is consistent with the stronger donor property of an amino group compared to a methoxy substituent, and further supports use of the 4′-CH_3 torsional barrier as a measure of 4-donor strength. The barrier deduced for origin I, which was postulated to involve the stronger donor, is ≈ 10% lower than that of origin II (i.e. 93 versus 104 cm^{-1}, respectively).

Based on the spectroscopic evidence, SS assigned the conformers as in Fig. 1. However, considering that the electronic perturbations are not fully understood, it is desirable to test the above model by an independent method. Possibly the most direct approach is to assign the moments of inertia to the species responsible for the origins I and II in each case.

Both high-resolution frequency-domain spectroscopy and the equivalent time-domain technique of rotational coherence spectroscopy can obtain the structures of jet-cooled molecules and clusters. One limitation of the frequency-domain approach is that it requires an apparatus resolution approaching 10 MHz, including Doppler broadening. A potential limitation for the study of a species such as *t*-stilbene is that the homogeneous broadening due to the short excited-state lifetime of $\leqslant 3$ ns reduces the structural precision of a high-resolution experiment. Nonetheless, Pratt and co-workers elegantly used high-resolution spectroscopy to measure the moments of inertia of *t*-stilbene and its argon 1:1 complex [4,6]. Rotational coherence spectroscopy allows the use of picosecond time-domain equipment to measure structures, also including stilbene and its van der Waals complexes [3,7]. Although it has less precision than the high-resolution experiments, it is more readily applied to large molecules and their aggregates. This is because the technique is sensitive to energy level differences within a given rotational manifold, and thus depends less on spectral broadening, such as due to excited-state lifetimes. Also, it is independent of Doppler broadening. As we show here, it provides a ready means to compare the structures of *t*-stilbene derivatives. Significantly, the addition of substituents serves to increase the resolution of the technique. For example, we will show that addition of a methyl group at the 4-position in MoS (i.e. the difference between that molecule and MoMeS) increased the recurrence time by ≈ 700 ps (i.e. 20–25%).

In the present application, interest fixes on the orientation of a single substituent group on the *t*-stilbene molecule. Simulations based on a calculated structure predicted that the rotational recurrence spacings for the two rotamers of MoS should differ by 30 ps. This equals 1% of the total value of $(B+C)^{-1}$ for this nearly prolate symmetric top.

2. Experimental section

MoS was available commercially at sufficient purity for immediate use. The derivative MoMeS was prepared by adding one equivalent of the Arbusov product $CH_3–C_6H_4–CH_2–P = O(OEt)_2$ to two equivalents of NaH in DME. One equivalent of *p*-anisaldehyde was added, and the mixture refluxed at 70° C for 30 min. The reaction was quenched with water and the resulting product recrystallized twice in ethanol and dried with an overall yield of ≈ 75%.

Measurements of fluorescence lifetimes and rotational coherence phenomena via picosecond time-correlated single-photon counting (TCSPC) have been described in the recent literature [8,9]. Briefly, the second harmonic of a 76 MHz mode-locked Nd^{3+}-YAG laser synchronously pumped a cavity-dumped dye laser using DCM in a mixture of benzyl alcohol and ethylene glycol. A second dye jet, containing the saturable absorber DQTCI in the same solvent mixture, controlled the pulse widths. The dye laser output consisted of tunable pulses at 3.8 MHz having autocorrelation width $\leqslant 10$ ps at 640 nm. After frequency doubling in $LiIO_3$, the effective bandwidth near 320 nm was $\leqslant 5$ cm^{-1}. The instrument response function, detected through a double monochromator via a Hamamatsu R2809U photomultiplier tube and Tennelec single photon counting equipment, was ≈ 38 ps (fwhm).

The supersonic helium jet, pulsed at ≈ 25 Hz, yielded 2 ms pulses through a 0.76 mm orifice. Samples were maintained at ≈ 110° C.

3. Results and discussion

Fig. 1 shows the fluorescence excitation spectra of MoS and MoMeS in the $S_0 \rightarrow S_1$ region near 325 nm. As described above, the presence of two electronic-origin transitions in each case reflected the presence of syn and anti conformations of the methoxy group. The electronic origin wavenumbers of all origin bands are given in Table 1 with the fluorescence lifetimes. Measured fluorescence decay times differed by ≈ 3% between two conformers of the same molecule and by ≈ 5% between molecules. Although these differences are close to the limit of our experimental accuracy for curve fitting, they were consistently measurable in repeated experiments.

To assign the two origin bands to the syn and anti conformers in each case, we carried out rotational coherence measurements using linearly polarized excitation and detection. Fig. 2 shows a representative experimental trace for MoS at 11.6 ps per channel. One positive and two negative recurrences are visible at $\leqslant 5$ ns in the fluorescence decay. The shape and alternating polarity are consistent with J-type recurrences, as expected for molecules of this type. The transient intensities are consistent with the high rotational symmetries (i.e. close to the prolate symmetric top limit) and compare with earlier work on *t*-stilbene [7,10,11]. One may observe a difference in recurrence time of approximately 40 ps at the first positive recurrence near 3.0 ns. To extract the maximum amount of data, measurements were extended to 10 ns for both molecules. This is equivalent to 2–3 recurrence cycles, and more than three times the fluorescence lifetime. This led to three positive and three negative transients for MoS and two positive and three negative transients for MoMeS.

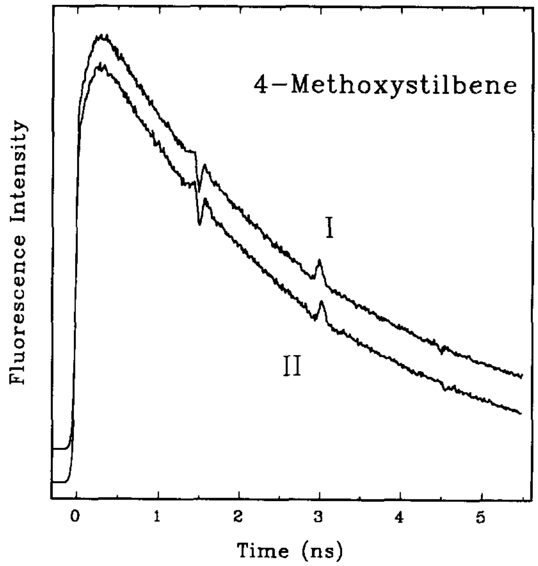

Fig. 2. Polarized fluorescence time profiles for MoS, showing displaced traces for two conformers.

The corresponding residual traces for both molecules and all four conformers are shown in Figs. 3 and 4 (time resolution = 23.2 ps per point). Since the recurrence times between conformers differ by only 1%, we present as a visual aid a difference trace for each molecule. The sequence of derivative transients of alternating sense is consistent with the alternating sign of the recurrence transients and the difference in their separation between the two conformers. From the original traces, a linear regression analysis yielded the time difference of the *J* recurrences for all species, as given in Table 2. The relative precision is about 5 ps. However, the absolute precision is limited by the time axis calibration of about 0.7%, yielding an absolute uncertainty of > 20 ps at 3 ns. Since the *J* recurrence time corre-

Table 1
Fluorescence characteristics of methoxy-*t*-stilbenes

Species	Isomer [a]	0_0^0 position (cm^{-1})	Fluorescence lifetime (ns)
4-methoxy-	I	30744	2.98
4-methoxy-	II	31023	2.88
4-methyl,4′-methoxy-	I	30517	2.83
4-methyl,4′-methoxy-	II	30783	2.72

[a] In this work, we determine that isomer I is the syn isomer, and that isomer II is the anti isomer.

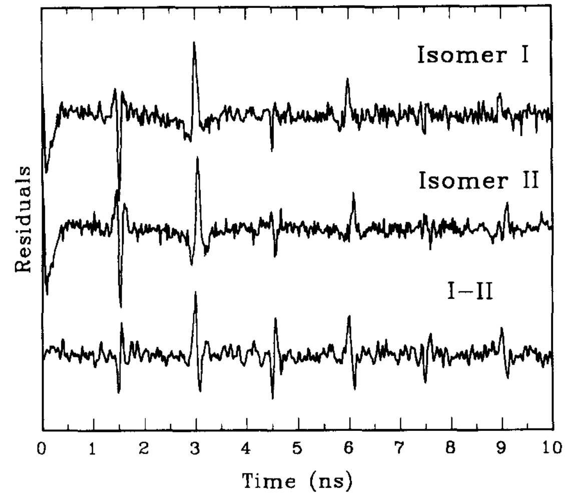

Fig. 3. Residual traces for the two conformers of MoS, with a difference trace highlighting the subtle difference between the two. These traces were normalized to constant noise level.

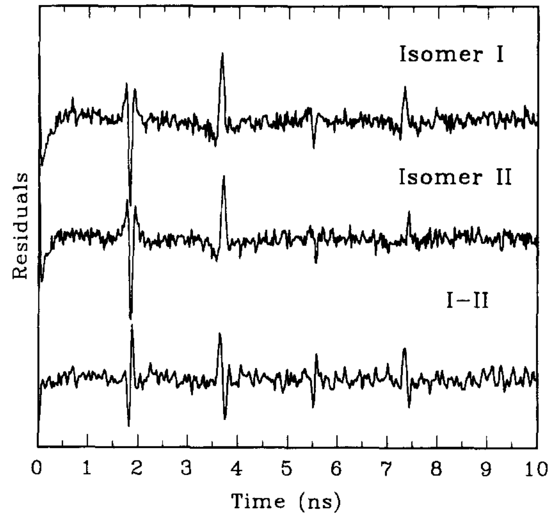

Fig. 4. Residuals traces for the two conformers of MoMeS, as in Fig. 3.

sponds to the inverse of the sum of the rotational constants B and C, these values are included in Table 2.

Having obtained some structural information, a definite assignment of the conformer resonances is possible by comparing calculated structures with the experimentally obtained sum of the B and C rotational constants. AMPAC calculations using the AM1 Hamiltonian predict two stable, planar conformers, from which calculated sums of B and C are given in Table 2. The assigned structures are inset in Fig. 1 labelling the corresponding electronic-origin resonances.

The assignment of the syn and anti conformers involved two main assumptions. First, apart from the rotation of the methyl group, the bulk of the molecule was assumed rigid. This is consistent with the results of the AMPAC calculations, which predict a small shift in the position of the oxygen atom. However, the present case of methyl location is unlike the more critical case of 1-naphthol. There, oxygen motion complicated the assignment of hydrogen atom positions in the two conformers [12]. Also, the AMPAC calculation was specific to the electronic ground state, whereas the measurements correspond to the excited state. However, the spectra suggest little

Table 2
Rotational coherence data for S_1 4-methoxy-*t*-stilbenes

Species	Recurrence time (ns)	Rotational constants ($B + C$) (MHz)	
	experimental [a]	AMPAC calculation [b]	experimental
4-methoxy-*t*-stilbene			
isomer I (325 nm)	2.990 ± 0.003	331.3	334.4 ± 0.3
isomer II (322 nm)	3.032 ± 0.003	328.0	329.8 ± 0.3
	diff. = 0.042 ± 0.006		
4-methyl,4′-methoxy-*t*-stilbene			
isomer I (327.7 nm)	3.668 ± 0.002	270.8	272.6
isomer II (324.8 nm)	3.712 ± 0.003	268.2	269.4
	diff. = 0.044 ± 0.005		

[a] Absolute calibration accuracy ≈ 0.7%. Relative calibration accuracy between isomers of the same species, < 10 ps.
[b] Calculated values for the electronic ground state.

difference in structure between the ground and excited states, apart from the known methyl torsional behavior of MoMeS. This discrepancy may account in part for the systematic difference between the calculated and experimental results, but again should not affect the ordering of the results for the two conformers.

4. Conclusions

The existence of two conformers having significantly different S_1 energies in MoS and MoMeS is consistent with previous knowledge of the *t*-stilbene system. The 150 cm^{-1} threefold activation barrier in the excited state of 4-methyl-*t*-stilbene indicates a difference in π-electron density at the two adjacent meta sites. Presumably this difference also exists in *t*-stilbene. The lower energy methoxy conformer likely has the lone pair cis to the more electron-deficient 3-position. The present work has found that the syn methoxy isomer is lower in energy, which places the lone pair position anti to the ethylene group. This, in turn, suggests that the anti 3-position is relatively electron deficient and the syn 3-position is relatively electron rich. Given that the π-electron density asymmetry of the 3-position must originate from placement of both the double bond and remote ring off the para axis of the substituted ring, and that both the π-rich groups lie on the syn side, this result is intuitively reasonable.

Acknowledgements

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