LETTERS TO THE EDITOR

COMMUNICATIONS

Doppler-free time-resolved polarization spectroscopy of large molecules: Measurement of excited state rotational constants

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Measurement of the rotational spectra and constants of molecules can be a powerful probe of excited state geometries and intramolecular dynamics. The conventional approach for obtaining rotationally resolved spectra is to use high-resolution (frequency domain, time-integrated) laser excitation. For medium-sized molecules, recent advances in these high-resolution techniques have made it possible to obtain Doppler-free spectra of benzene[1] (using two-photon excitation), and jet-cooled spectra of tetrazines,[2] pyrazine,[3] and others.[4] These results on *medium-sized* molecules have provided valuable information on geometries,[1,2] and on the dynamics of intramolecular singlet–triplet coupling[3,5] and the "channel 3" decay in benzene.[1] For large molecules, to obtain rotationally resolved spectra one needs stable, ultranarrow bandwidth lasers together with a scheme to reduce Doppler broadening to less than several megahertz.

In this Communication we report the first application of a *time-resolved polarization* technique to the study of the rotational constants and geometries of large molecules. The technique (1) is Doppler-free, or, more accurately, Doppler insensitive (one-photon excitation), (2) allows one to measure excited state rotational constants directly, (3) can provide information pertaining to absorption and emission transition dipole directions, and (4) can be readily applied to large molecules. Results are reported here for *t*-stilbene, *t*-stilbene-d_{12}, and *t*-stilbene–argon complexes. For each of these molecules (isolated by jet cooling[7]) we report values of the rotational constants $\frac{1}{2}(B + C)$ and compare these values with calculated ones. The results amply demonstrate the power of this probe of excited state rotational level structures.

The principle of the technique is as follows. A polarized picosecond pulse coherently prepares excited state S_1 rotational levels of individual molecules in the sample. This creates an initial alignment of excited molecules. By viewing the fluorescence with an analyzer one is able to time resolve the dephasing and rephasing of this alignment. Because the

energy spacings of the coherently prepared rotational levels are *commensurate* [e.g., for parallel-type absorption in a symmetric top molecule, the spacings are $2BJ$, $2B(J + 1)$, and $2B(2J + 1)$], the rephasing, which results in a decrease or increase in the fluorescence intensity depending on the relative polarization of excitation and fluorescence detection, is manifested as transients at times determined by the rotational constants of the molecule. For parallel-type transitions in a symmetric top the recurrences occur at time intervals of $1/(2B)$. For parallel transitions in near prolate asymmetric tops, such as *t*-stilbene, they occur at intervals of $1/(B + C)$. Thus from these recurrences one can directly obtain rotational constants. The transients associated with the rotational motion can be suppressed by using magic angle (54.7°) detection, just as is done in liquids.[8]
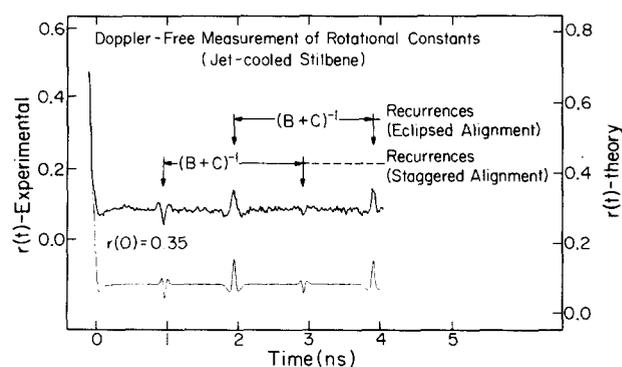

FIG. 1. Fluorescence anisotropy $r(t) \equiv [I_{\parallel}(t) - I_{\perp}(t)]/[I_{\parallel}(t) + 2I_{\perp}(t)]$ for the 0_0^0 absorption and fluorescence transition of *t*-stilbene. Top—experimental $r(t)$: expansion orifice 70 μm, 75 psig Ne backing pressure, laser-to-nozzle distance 3 mm, nozzle $T = 150$ °C. Bottom—simulated $r(t)$ calculated (Ref. 9) assuming rotational constants $A = 0.089\,267$, $B = 0.008\,767$, and $C = 0.008\,333$ cm^{-1}, fluorescence lifetime of 2.6 ns, [Ref. 7(a)] jet $T = 5$ K, and accounting for the finite temporal detection response. Transients occur at times when the alignment of the emission dipoles of molecules in the sample is "eclipsed" (i.e., along the direction of the excitation polarization) or when the alignment is "staggered" (biased toward 90° relative to the excitation polarization).

TABLE I. Recurrence times and rotational constants measured by the Doppler-free technique.

Molecule		Energy (cm^{-1})	Recurrence time (ns)	Rotational const. $\dfrac{B+C}{2}$ (cm^{-1})	
				Measured	Calculated
t-stilbene-h_{12}		0($\equiv$32 234 cm^{-1})	1.951 $\pm$ 0.010	0.008 54 $\pm$ 0.000 04	0.008 42
t-stilbene-h_{12} (vib.)		$+$ 83	1.954 $\pm$ 0.020	0.008 53 $\pm$ 0.000 09	
t-stilbene-d_{12}		$+$ 93	2.140 $\pm$ 0.012	0.007 79 $\pm$ 0.000 05	0.007 70
t-stilbene-Ar:					
	1)	$-$ 40	2.384 $\pm$ 0.064	0.006 99 $\pm$ 0.000 20	0.006 67[a]
	2)	$-$ 63	2.410 $\pm$ 0.040	0.006 91 $\pm$ 0.000 12	

[a] The principal A axis of inertia is very close to that of t-stilbene ($\sim 10°$).

There are two unique features of the above scheme. First, the picosecond temporal resolution allows for observation of the transients, which can have widths on the order of 10 ps or less. Second, thermal effects (arising from the initial population of J, K levels in S_0) do not wash out these recurrences. This is because of the commensurability of beat frequencies for a symmetric top or near commensurability for an asymmetric top.[9,10]

Our experimental apparatus has been described in detail elsewhere.[11] Briefly, we measure the decay of spectrally resolved, polarization-analyzed fluorescence that emanates from a jet-cooled sample upon excitation with the linearly polarized, frequency-doubled output of a picosecond dye laser (synchronously pumped, cavity dumped). Decays and recurrences are measured using time-correlated single-photon counting. For this work the temporal response of the detection system was typically 45 ps.

Figure 1 shows experimental results corresponding to the excitation of the S_1-0_0^0 band[7(a)] of t-stilbene at 32 234 cm^{-1} and detection of the same fluorescence band. [Note that rotational structure[12] is not resolved by the excitation laser (bandwidth $\sim$ 5 cm^{-1}) nor by the detection monochromator.] The data are presented as the polarization anisotropy, $r(t)$, calculated directly from observed decays ($I_\parallel$ and $I_\perp$) *without deconvolution of the detection* response function. Also included in the figure is a simulation of the data calculated using known parameters for t-stilbene[12,13] and expressions for $I_\parallel$ and $I_\perp$.[9,10] In the figure one can see clearly the recurrences associated with thermally averaged rotational coherence. The spacings between recurrences in the experimental traces determine directly the average of the rotational constants B and C. The value so obtained for the 0^0 level of t-stilbene is given in Table I. It agrees well with the value calculated using the geometry of Ref. 14.

We have also made measurements on t-stilbene S_1 vibrational level at 83 cm^{-1},[7] t-stilbene-d_{12} S_1-0^0 level, [7(a)] and on the t-stilbene–argon van der Waals complex bands[7(c)] occurring at $-$ 40 and $-$ 63 cm^{-1} shifts with respect to the t-stilbene 0_0^0 band. The rotational constants derived from these measurements appear in Table I, and compare well with calculated values. The calculated value for the argon complexes was obtained by assuming the same t-stilbene geometry as above, with one argon atom placed 3.45 Å[15] above one of the phenyl groups and on the inner side of that moiety (the phenyl groups are tilted about 30° out of the plane de-

fined by the ethylene group[14]). Notably, calculations based on the assumption of two argon atoms yield significantly lower $(B + C)/2$ values ($\sim$0.0052 cm^{-1}) than those obtained from experiment.

In conclusion, we have presented results that demonstrate the usefulness of time-resolved, Doppler-free polarization techniques in studying the rotational level structures of large molecules. This technique should be applicable to a wide variety of problems associated with the spectra and dynamics of the excited states of large molecules.

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[5] Other studies using quantum beats on similar systems have provided similar important information about intramolecular couplings (see, e.g., Ref. 6). We will not concern ourselves here with such couplings. Nor are we concerned with the effect of picosecond energy redistribution [Refs. 16(a) and 16(b)] or singlet–triplet coupling [Ref. 16(c)] on $r(t)$.

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The methyl rotor as an accelerating functional group for IVR

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Recent S_1 *p*-difluorobenzene (*p*DFB) studies revealed that the lowest frequency mode, an out-of-plane fluorine bend ν_{30}, is an accelerating mode for intramolecular vibrational redistribution (IVR).[1-3] Evidence is presented here to show that IVR can also be accelerated by a functional group. The effect is seen in S_1 *p*-fluorotoluene (*p*FT), a molecule in which a fluorine of *p*DFB has been replaced by a methyl group.

Comparisons of the S_1 level structures of *p*DFB and *p*FT suggest that methyl substitution would minimally effect IVR for S_1 levels below about 1500 cm^{-1}. The methyl group has little interaction with the ring, being nearly a free rotor with a barrier of only about 5 cm^{-1}.[4-6] Thirty of the remaining 38 vibrational degrees of freedom match the 30 *p*DFB fundamentals with almost no frequency change.[7] The remaining *p*FT modes are methyl vibrations. Three are near 1100 cm^{-1} and the rest are above 2700 cm^{-1}.[7] Thus aside from the "free-rotor" states, the S_1 vibrational level structure and the total vibrational level densities in these molecules are closely parallel for energies to about 1500 cm^{-1}.

The spectroscopies are also parallel. At resolution that reveals vibrational structure but not band contours, the $S_1 \leftarrow S_0$ absorption spectra are almost superimposable.[8,9] The $S_1 \rightarrow S_0$ fluorescence spectra from the 0° level are also replicas, either at 300 K or from a cold expansion.[10] These spectroscopies do not reveal either the *p*FT methyl vibrations or rotation. The molecules are nearly identical twins, and similar ring excitations can be produced in each. Thus the pair provides a surgical opportunity to observe the specific effect of a methyl rotor on IVR dynamics.

The 300 K fluorescence spectra from higher S_1 levels begin to reveal the effect. Those spectra show that the molecules are qualitatively different. Figure 1 displays 300 K fluorescence spectra taken under comparable conditions from a series of analogous S_1 levels. Discrete vibrational structure from the pumped level dominates *p*DFB fluorescence, even with $\epsilon_{vib} > 1600$ cm^{-1}. The *p*FT fluorescence is completely different. Resonance structure is essentially gone when excitation has climbed to levels near 1600 cm^{-1}. The difference is not merely due to thermal inhomogeneous broadening

since that contribution to fluorescence congestion is comparable for the two molecules. We are observing a genuine effect of greatly enhanced level mixing within the S_1 state of *p*FT.

Fluorescence with picosecond time resolution imposed by chemical timing has revealed dynamic IVRs in both *p*FT[11,12] and *p*DFB.[13,14] Those in S_1 *p*DFB have been characterized for 11 levels with $\epsilon_{vib} = 1615 - 3310$ cm^{-1} where IVR lifetimes run from 16 to 290 ps.[1] Some are listed in Table I. That table also includes five *p*FT IVR lifetimes recently obtained by similar timing experiments.[8] Although
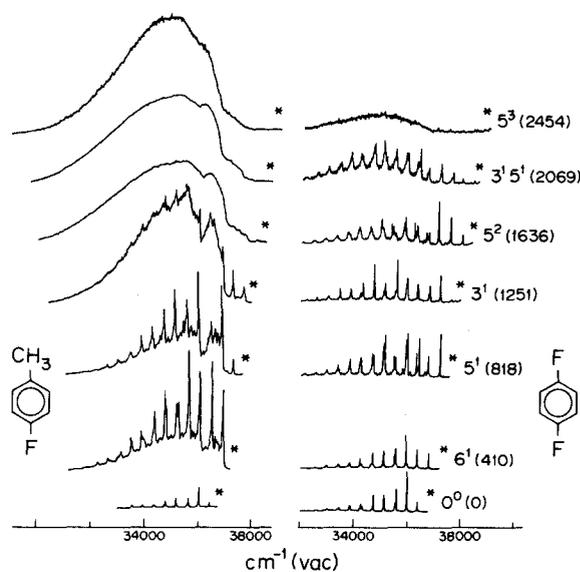

FIG. 1. Resolved 300 K collision-free fluorescence spectra from *p*FT and *p*DFB showing the presence or absence of vibrational structure after excitation of various S_1 levels. The vibrational identities (Ref. 19) of the *p*DFB levels are given with S_1 level energies in parentheses. The corresponding *p*FT spectra are from levels of the same vibrational identity (except 3^2 at 2385 cm^{-1} is excited in *p*FT instead of 5^3). The *p*FT energies are given in Table I (6^1 in *p*FT is 398 cm^{-1}). The fluorescence resolution is generally about 25 cm^{-1}. Excitation positions are marked with asterisks. The horizontal scales are approximately the same for each molecule. Vertical scales are exaggerated for *p*FT relative to *p*DFB, except for the 0° spectrum. *p*DFB spectra are from Ref. 13.