

Spectroscopy and dynamics of jet-cooled 4-dimethylamino-4'-cyanostilbene in the S_1 state

Rainer Daum, Tony Hansson¹, Ralf Nörenberg, Dirk Schwarzer, Jörg Schroeder

Abteilung Spektroskopie und Photochemische Kinetik, Max-Planck-Institut für Biophysikalische Chemie, Am Faßberg, D-37077 Göttingen, Germany

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Abstract

The S_1 state of jet-cooled 4-(N,N-dimethylamino)-4'-cyanostilbene (DCS) was studied by picosecond fluorescence spectroscopy. The line structure of the $S_0 \rightarrow S_1$ -excitation spectrum is a superposition of transitions characteristic of isolated trans-stilbene and the dimethylamino group. Rotational contour analysis and rotational coherence spectroscopy suggest a non-planar geometry of DCS in both electronic states. Fluorescence decays are monoexponential up to 3700 cm^{-1} above the origin at 27038 cm^{-1} . The lifetimes vary little up to 733 cm^{-1} ($\langle \tau \rangle = 2.097 \text{ ns}$) and start to decrease above this energy because of the onset of photoisomerization. An RRKM-fit to the non-radiative rate coefficients yields a barrier height $E_0 = 745 \text{ cm}^{-1}$.

1. Introduction

The influence of the solvent environment on the dynamics of elementary chemical reactions is at the focus of current experimental and theoretical research, as ultrafast laser techniques as well as powerful computers allow the real time study of the complex dynamics caused by the interaction between an excited solute molecule and the surrounding solvent shell. Many reactions investigated by these means involve barrier crossing processes over a relatively small potential barrier which may be modified by

solute-solvent interactions. A prominent example is the photoisomerization of trans-stilbene (*t*S) on the S_1 -potential energy surface which has been studied under a great variety of physical conditions [1–3]. One major point of interest in this system has been the height E_0 of the potential barrier to photoisomerization in the S_1 state in the isolated molecule and its apparent decrease as a consequence of solvent effects. While for isolated *t*S one obtains $E_0 \approx 1200$ – 1300 cm^{-1} from the energy dependence of specific rate coefficients $k(E)$ [4,5], in supercritical ethane at very low viscosity we determined $E_0 = 700 \text{ cm}^{-1}$ from the temperature dependence of the high pressure rate coefficient k_x [6]. Recently, we found evidence for a corresponding decrease of the barrier height to approximately 900 cm^{-1} in jet-cooled 1:1-solvate-complexes of *t*S with *n*-hexane [7]. Whether

¹ Present address: KTH, Fysik 1, S-100 44 Stockholm, Sweden.

this reduction of the apparent barrier height is a dynamic effect, involving the acceleration of intramolecular vibrational energy redistribution (IVR) in tS by solute–solvent interactions [8,9], or a static effect in the sense that the reaction field of the polarizable environment causes a reduction of electron density in the central double bond [6,10], is still an open question which we want to investigate further by studying the dynamics of jet-cooled solvent clusters of the stilbene derivative trans-4-(N,N-dimethylamino)-4'-cyanostilbene (DCS) in a supersonic jet following excitation to the S_1 state. As a first step in this direction, we measured the fluorescence excitation and emission spectra as well as the energy dependence of the fluorescence lifetimes of jet-cooled isolated DCS to investigate the influence of the substituents on the barrier height and test the applicability of statistical reaction rate theories. The influence of highly polar 'push–pull' 4,4'-substitution will be compared with that reported for alkyl- [11] and methoxy-substituents [12].

The dual fluorescence of DCS observed in polar solution has led to the suggestion that upon excitation to a 'locally' excited S_1 state (LE) in polar solvents this molecule forms a twisted intramolecular charge transfer state (TICT) [13–15]. In this sense DCS, in addition to being a derivative of stilbene, also shows characteristics similar, e.g. to the most prominent 'TICT-molecule' 4-(N,N)-dimethylamino)-benzonitrile (DMABN). Though jet-cooled isolated DMABN, as expected, shows no spectral evidence for TICT-formation, the change of the fluorescence spectra upon complexation may indicate a possible involvement of the TICT state [16–21]. It will be instructive to investigate the spectra and dynamics of isolated and complexed DCS in this respect and compare it with those of DMABN.

In DCS, therefore, we can expect, under the influence of a changing solvent cluster size and type, a competition [14] between two routes of S_1 -deactivation: adiabatic photoisomerization and deactivation via a TICT-like channel which should be accompanied by corresponding changes in the fluorescence spectra. As a first step, we present here our results on the fluorescence spectroscopy and dynamics of isolated DCS. Investigations of 1:1-complexes of DCS with polar solvent molecules will be the subject of a subsequent article.

2. Experimental

Details of the experimental setup will be published elsewhere. Here we give only a brief description of the expansion conditions, the excitation sources, and the time correlated single photon counting system.

Cold DCS was prepared in a continuous free jet expansion with He as the carrier gas. The nozzle was fitted with a circular pinhole of 100 μm diameter and heated to about 160–210°C. The typical backing pressure was 4 bar. The vacuum chamber was pumped by a 3500 l/s diffusion pump (Edwards EO 400/7000 with CB400) backed by a roots pump (Edwards EH250/E2M40), yielding an effective pumping rate of 3100 l/s and maintaining a background pressure of about 1 μbar during measurements.

Excitation spectra were taken with an excimer laser-pumped dye laser (Lambda Physik LPX 100/Scanmate 2) using DMQ as the laser dye. The maximum pulse energy used was 8 mJ at 370 nm, the pulse duration 15 ns, and the spectral bandwidth of the laser 0.15 cm^{-1} . The laser beam crossed the jet about 2–3 mm downstream of the nozzle. The fluorescence was collected at right angles to laser and molecular beam by a gated photomultiplier tube (Hamamatsu 1P28).

Emission spectra were recorded by exciting DCS with pulses from a tunable synchronously pumped picosecond dye laser (pump source Quantronix mode-locked Nd:YLF laser). Using DCM Spezial or Pyridin 2 (Lambda Physik dyes) and a lithiumiodate crystal for frequency doubling we obtained 3 mW cw-power at 369.8 nm at a laser spectral bandwidth of 4.5 cm^{-1} . The fluorescence was focused onto the entrance slit of a monochromator (SPEX 500M, 1200 lines/mm, 400 nm blaze) and detected by a MCP-PMT (Hamamatsu R2809U) in photon counting mode (photon counter Stanford Research SR400).

Fluorescence lifetimes were determined by time correlated single photon counting using the same excitation source as for emission spectroscopy. For this purpose the output of the MCP-PMT was amplified (bandwidth 1 GHz, 20 dB gain) and fed into the custom adapted input of a CF-discriminator (Tennelec TC 454) to provide the start-pulse in an inverted setup using a second CFD to provide the stop pulse

derived from a photodiode monitoring the laser output, and a time-to-amplitude converter (Tennelec TC864). After subsequent A/D-conversion (Nuclear Data ND582) the TAC-output was stored via DMA-mode in a PC for analysis. The fwhm of the apparatus response function was ≤ 70 ps. For rotational coherence spectroscopy the apparatus was equipped with the appropriate polarizers in the fluorescence detection path.

DCS was prepared in a Wittig reaction [22] and subsequently recrystallized. The isomers were separated chromatographically, and trans-DCS was vacuum sublimed before use.

3. Results and discussion

3.1. LIF excitation and emission spectra

The LIF excitation spectrum of jet-cooled DCS ($p_{\text{HE}} = 4$ bar, nozzle temperature 160°C) in Fig. 1a shows a highly congested spectrum at excitation energies above 29000 cm^{-1} . At higher nozzle temperatures hot bands appeared below the lowest energy transition at 27038 cm^{-1} . Comparison with the corresponding LIF emission spectrum in Fig. 1b obtained with excitation at $\lambda_{\text{vac}} = 369.95\text{ nm}$ suggests that this transition may be identified with the $S_0 \leftarrow S_1, 0_0^0$ transition of isolated DCS. The rich line structure in the region up to 200 cm^{-1} above the origin of the excitation spectrum is caused by the combination of the low frequency modes of the stilbene-like backbone and the torsion and inversion vibrations of the dimethylamino group. In the following we will only address the main features of the spectra. A detailed discussion of the proposed assignments will be given elsewhere [27].

The low energy region of the LIF excitation spectrum shows strong transitions at $50, 69, 90, 118, 130, 153, 171, 174, 180, 198$ and 202 cm^{-1} . At first we compare these with correspondingly strong lines present in *tS* in about the same energy range above the origin [4,7,24–26]. The most prominent vibration in the LIF excitation spectrum of DCS appears at 131 cm^{-1} with an overtone at 262 cm^{-1} . We assign this transition, by analogy with *tS* [4,23,24], 4-methyl-4'-methoxy-trans-stilbene [28], and 4-methyl-4'-amino-trans-stilbene [29] as 25_0^1 , the totally sym-

metric in plane phenyl wag. This assignment is consistent with the estimated mass effect on the vibrational frequency caused by substitution of the 4- and 4'-hydrogen atoms in stilbene with the cyano and dimethylamino group, respectively [27]. The inten-

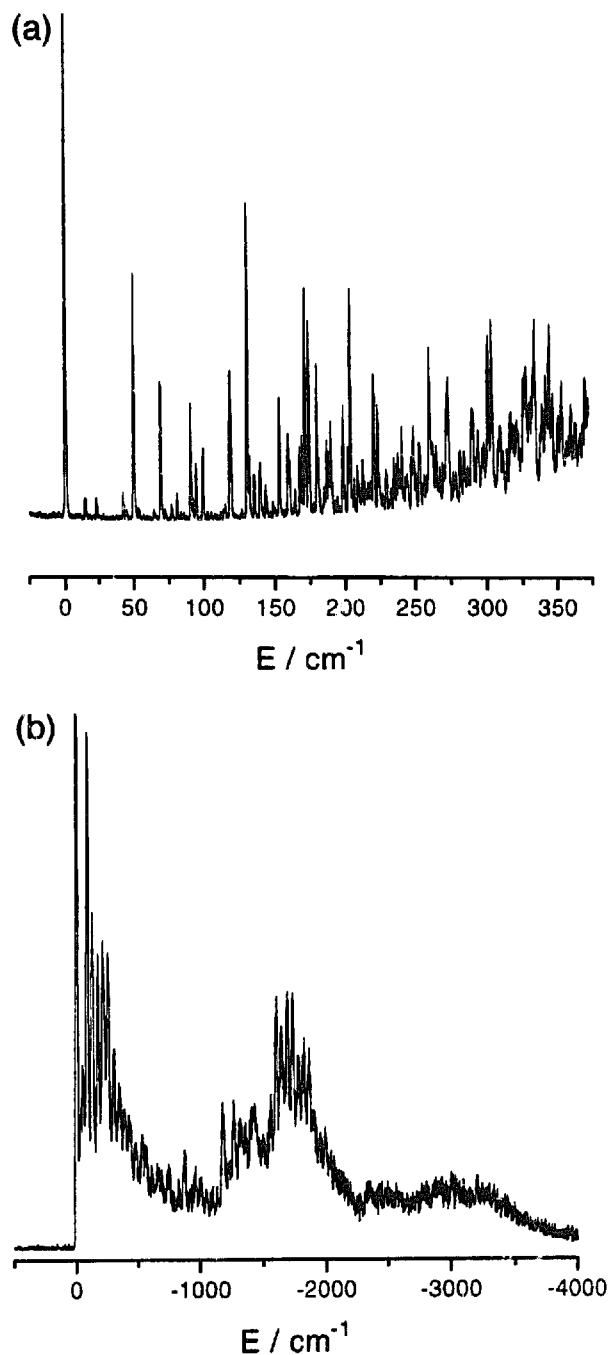


Fig. 1. (a) LIF excitation spectrum of jet-cooled isolated DCS. (b) LIF emission spectrum of jet-cooled isolated DCS.

sity of this transition would suggest that the $S_1 \leftarrow S_0$ transition moment of DCS lies in the molecular plane. The same mass effect also leads to the red shift of the 24_0^1 transition [28,29] (C_e -phenyl bend) appearing at 278 cm^{-1} in tS to 202 cm^{-1} in DCS [27]. A mode that seems to be only slightly affected by 4,4'-substitution is the out-of-plane phenyl torsion, ν_{37} [28,29]. Hence we tentatively assign the 90 and 181 cm^{-1} transitions as 37_0^2 and 37_0^4 , respectively. The less intense line at 42.5 cm^{-1} we attribute to 36_0^2 , the phenyl flap mode.

In addition, one can identify transitions characteristic of the dimethylamino group as they appear in the LIF excitation spectra of, e.g., DMABN or dimethylaniline, because they seem to be largely unaffected by the remainder of the intramolecular environment [30]. These are the rotation and inversion vibrations at $81, 132, 169 \text{ cm}^{-1}$ and $119, 188, 198 \text{ cm}^{-1}$, respectively.

The assignment of the other low frequency modes is unclear. Possibly the very strong lines at 50 and 69 cm^{-1} for which we also find overtone and combination bands [27] correspond to ring motions on a torsional potential energy surface modified by the presence of the cyano and dimethylamino groups [28].

Inspecting the LIF emission spectrum in the region up to 400 cm^{-1} , taken with a spectral resolution of 4.5 cm^{-1} , reveals six low frequency normal modes at $22, 29, 48, 83, 121,$ and 129 cm^{-1} in the S_0 state. The line pattern observed in this spectral region is repeated with medium intensity at 1180 cm^{-1} and again with strong intensity at 1610 cm^{-1} . An analysis of the LIF emission spectrum will be given in Ref. [27].

3.2. Rotational constants of DCS in S_1 and S_0

We used the method of rotational coherence spectroscopy [31,32] to obtain information about the rotational constants of DCS in the S_1 state. Fig. 2 shows the fluorescence anisotropy decay of jet cooled DCS after excitation of the $\nu(0_0^0)$ band which shows a recurrence time of the anisotropy transient of $4.94 \pm 0.02 \text{ ns}$. This leads to a value of $0.00675 \pm 0.00002 \text{ cm}^{-1}$ for the sum of rotational constants B and C for DCS in the S_1 state. The initial anisotropy $r(t=0)$ is 0.35 , i.e. close to the maximum value of

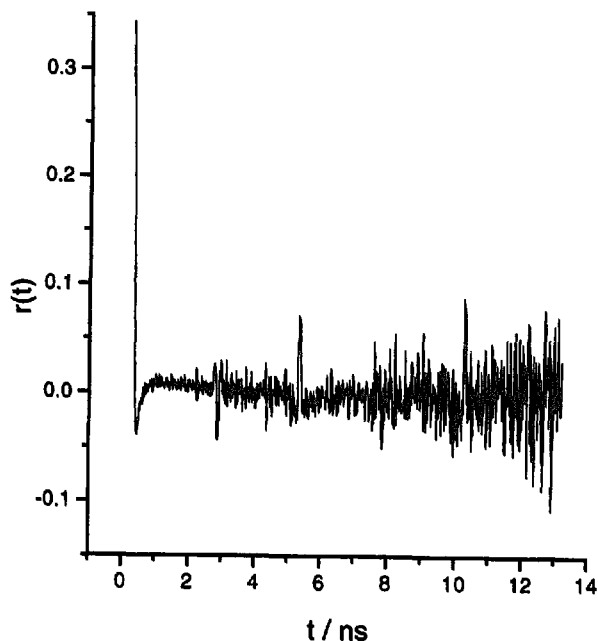


Fig. 2. Fluorescence anisotropy signal of isolated DCS.

0.4 , indicating that (i) the transition dipole moment and the principle axis of the largest moment of inertia are almost parallel to each other, and (ii) that the asymmetry, i.e. the difference between B and C , is 6% at most [27,31].

Additional information about rotational constants can be obtained from an analysis of the rotational contour [33,34] of the $\nu(0_0^0)$ band shown in Fig. 3 which has a half width of 0.75 cm^{-1} . The rotational constant A in S_0 was estimated from semiempirical geometry optimization [35] as 0.00660 cm^{-1} , and a simulation using the Hönl–London equation with fit parameters A in S_1 , B and C in S_0 , and the rotational temperature T_R yielded the lineshape function given as a dashed line in Fig. 3, assuming a transition dipole moment parallel to the main axis. While the value of $T_R = 8 \text{ K}$ can be regarded with confidence, the rotational constants in S_0 obtained in this way have to be considered as preliminary [27]. Table 1 summarizes the rotational constants determined by rotational coherence spectroscopy and lineshape simulation. Included is also a calculation of the rotational constants for a planar geometry of DCS in S_0 . The calculated value of $B + C$ is by 3% larger than the one obtained from the rotational contour simulation which would suggest a nonplanar conformation

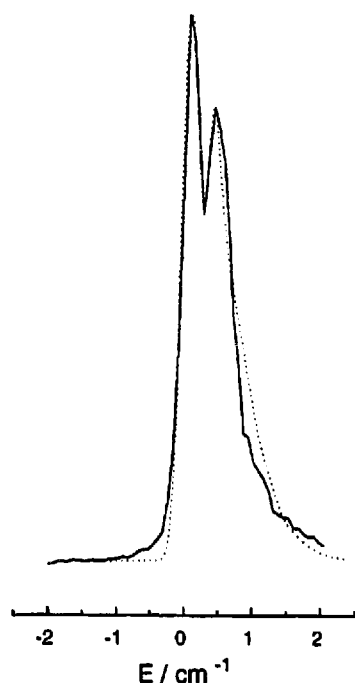


Fig. 3. Rotational contour of the $\nu(0_0^0)$ transition band of the LIF excitation spectrum of DCS (full line) and result of lineshape simulation (dashed line; see text).

of DCS in its ground state. It also exceeds the corresponding value in the S_1 state beyond the experimental error limit of 0.3%. On the other hand, the intensity of the $\nu(0_0^0)$ band indicates little conformational change of DCS upon excitation, so probably DCS has a nonplanar geometry also in the S_1 state [27].

Table 1

Rotational constants A and $B + C$ in S_0 and S_1 states of DCS from rotational coherence spectroscopy, rotational contour simulation, semiempirical geometry optimization and calculated for planar geometry in S_0

State	A (cm^{-1})	$B + C$ (cm^{-1})
S_0	0.00660 ^a	0.00663 ^b
S_0	0.00664 ^c	0.00681 ^c
S_1	0.00661 ^b	0.00675 ^d

^a Semiempirical geometry optimization.

^b Rotational contour simulation.

^c Calculated for planar geometry in S_0 .

^d Rotational coherence spectroscopy.

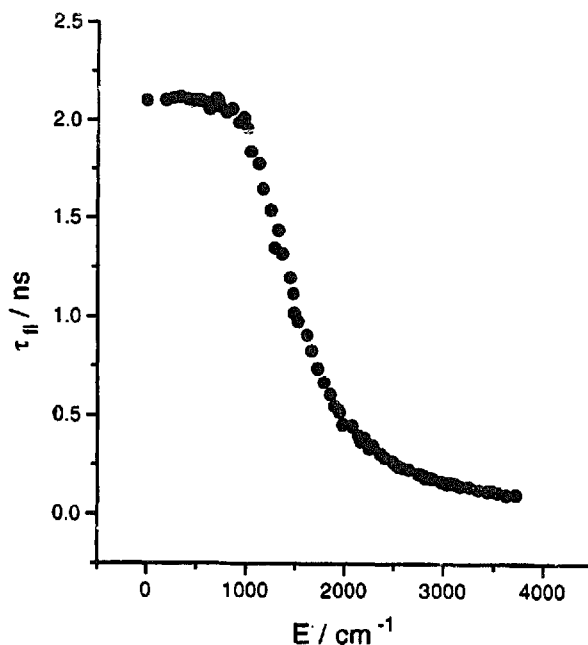


Fig. 4. Excess energy dependence of fluorescence lifetimes of isolated DCS.

3.3. Energy dependence of fluorescence lifetimes

Fluorescence decays were measured as a function of excitation energy up to excess energies E of 3700 cm^{-1} above $\nu(0_0^0)$ and found to be strictly monoexponential for all excitation energies. Considering the experimental time resolution this implies that there are no lifetime components $\tau_i > 15 \text{ ps}$. Fig. 4 shows a plot of the measured fluorescence lifetimes τ_f versus E . They are independent of excess excitation energy up to approximately 800 cm^{-1} and start to decrease rapidly with a further increase in E . This kind of energy dependence is typical for the onset of a nonradiative process controlled by an energy barrier in the excited state. Because of the similarity of the $k(E)$ -curves with those measured for tS [3–8] and similar molecules [12], we suggest that this process has to be identified with the motion along the trans–cis-photoisomerisation reaction coordinate in the S_1 state of DCS. A hypothetical route via a CT state can be safely ruled out for the isolated molecule, as this state would be expected to lie energetically above the ‘perpendicular’ state of DCS [36].

From the fluorescence lifetimes measured for low excess energies up to 733 cm^{-1} one obtains the

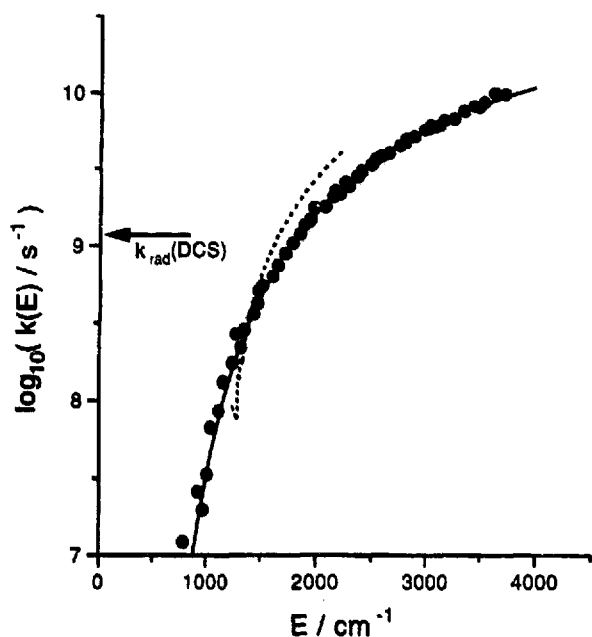


Fig. 5. Microcanonical rate coefficients $k(E)$ for trans-cis-isomerization of DCS in the S_1 state. (●, —) Optimized RRKM-fit to measured rate coefficients for DCS. (---) Optimized RRKM-fit to measured rate coefficients for tS [7].

average radiative lifetime for DCS, $\tau_{\text{rad}} = 2.097 \pm 0.016$ ns, which is assumed to be constant over the whole range of excitation energies up to 3700 cm^{-1} . Subtracting the average radiative rate coefficient from the measured fluorescence decay rate constants, one obtains the microcanonical rate coefficients $k(E)$ for S_1 photoisomerization plotted in Fig. 5. Considering the accuracy of the average radiative rate coefficient one can estimate the energy barrier of the photoisomerization channel in isolated DCS, $E_0 = 750 \pm 50 \text{ cm}^{-1}$.

If statistical theories apply for this reaction, one can obtain a more quantitative estimate of the barrier height from an optimized RRKM model fit [5] to the measured microcanonical rate coefficients $k(E)$. The normal mode spectrum of DCS in the S_1 state for this purpose was taken from the analysis of the LIF excitation spectrum (low frequency part up to 200 cm^{-1}) and force field calculations [35] (for the higher vibrational frequencies) resulting altogether in 99 vibrational modes [27]. Employing the Beyer-Swinehart algorithm [37] for state counting, taking 45 cm^{-1} as the frequency of the reactive mode (ν_{37} in accordance with corresponding calculations for tS

[5,38]), and scaling activated complex frequencies (all 38 modes with frequencies $\nu \leq 936 \text{ cm}^{-1}$) by a fit parameter F , we obtained best agreement with experiment (Fig. 5) for parameter values $F = 1.07$ and $E_0 = 745 \text{ cm}^{-1}$ [27] compared to $F = 1.05$ and $E_0 = 1260 \text{ cm}^{-1}$ for tS [7]. As is evident from the $k(E)$ -curve for tS included in Fig. 5, $k(E)$ values of DCS rise more slowly due to the higher density of states in this molecule.

The decrease of the barrier height in the S_1 state of DCS by about 40% with respect to tS is much larger than the effect deduced from quantum yield measurements in 4-alkyl-substituted tS (20% decrease for propyl) [11] and determined from $k(E)$ -measurements in 4-methoxystilbene (15% increase) [12]. A substantially higher barrier of about 3300 cm^{-1} was observed for the symmetrically substituted molecule dimethoxystilbene and explained in terms of an increased stabilization of the planar conformation of the S_1 state with respect to the twisted conformation [12]. In accordance with these propositions one may suggest that the smaller barrier in DCS is a consequence of a correspondingly increased stabilization of the 'perpendicular' state with respect to the planar conformation [36] which, as measured by the red shift of the $\nu(0_0^0)$ transition, is about 0.67 eV lower in energy than in tS . While upon motion along the reaction coordinate toward the twisted geometry tS is thought to become increasingly polar, the opposite is expected for DCS [36], leading perhaps to an effectively lower barrier. It is unclear, however, what kind of influence this reversal in the character of the electronic state precisely has on the barrier height E_0 .

It is curious to note that the barrier height of isolated DCS is about the same as that measured for tS in low viscosity supercritical fluids. One may speculate whether this is coincidental or an indication that the effect of strong 'push-pull' substitution on the S_1 -potential energy surface in the barrier region is similar to that of solvent cluster formation with tS . This would be somewhat surprising since the electronic properties of DCS and tS in the S_1 state are quite different.

An alternative interpretation of the decreased barrier in isolated DCS would be possible, if the barrier obtained from $k(E)$ -measurements of isolated tS was a consequence of incomplete IVR [8,9]. In this

case the smaller barrier in DCS could indicate that in this molecule IVR is almost complete on the timescale of reactive motion. This view would also be in accord with the absence of any short lived component in the measured fluorescence decay profiles for isolated DCS. The enhancement of IVR could be due to an increased coupling of the optically active modes to the dark states feeding the reactive mode, an assumption that would be supported by the significantly richer LIF spectrum of DCS in the low frequency region.

4. Conclusion

We presented LIF excitation and emission spectra of isolated DCS and assigned prominent lines of the low frequency part of the LIF excitation spectrum by comparison with corresponding spectra of *t*S and DMABN. The intensity of the line spectrum suggests that there is little conformational change upon excitation from S_0 to S_1 in DCS. From the analysis of the $\nu(0_0^0)$ rotational contour and rotational coherence signals we conclude that the molecule is nonplanar in both states. The energy dependence of the fluorescence lifetimes suggests the onset of a nonradiative process above 750 cm^{-1} excess excitation energy which we identify with the trans–cis-photoisomerization channel. An RRKM-analysis of the $k(E)$ data suggests that the process can be described by statistical theories, implying that IVR is complete on the timescale of motion along the reaction coordinate. Possible reasons for the lower energy barrier in DCS with respect to *t*S are the different nature of the S_1 -potential energy surface in DCS and the enhancement of IVR due to the presence of an increased number of optically active low frequency modes.

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References

- [1] J. Saltiel and Y.-P. Sun, in: Photochromism-molecules and systems, eds. H. Dürr and H. Bouas-Laurent (Elsevier, Amsterdam, 1990).
- [2] D.H. Waldeck, Chem. Rev. 91 (1991) 415; J. Molec. Liq. 57 (1993) 127.
- [3] J. Schroeder and J. Troe, in: Activated barrier crossing, eds. G.R. Fleming and P. Hänggi (World Scientific, Singapore, 1993) p. 206.
- [4] J.A. Syage, P.M. Felker and A.H. Zewail, J. Chem. Phys. 81 (1984) 4685, 4706.
- [5] J. Troe, Chem. Phys. Letters 114 (1985) 241.
- [6] J. Schroeder, Ber. Bunsenges. Physik. Chem. 95 (1991) 233.
- [7] C. Lienau, K. Wack and J. Schroeder, unpublished results.
- [8] S.H. Courtney, G.R. Fleming, L.R. Khundkar and A.H. Zewail, J. Chem. Phys. 80 (1984) 4559.
- [9] S. Nordholm, Chem. Phys. 137 (1989) 109.
- [10] J. Schroeder and J. Troe, Chem. Phys. Letters 116 (1985) 453.
- [11] K. Rademann, U. Even, S. Rozen and J. Jortner, Chem. Phys. Letters 125 (1986) 5.
- [12] L. Banares, A.A. Heikal and A.H. Zewail, J. Phys. Chem. 96 (1992) 4127.
- [13] A. Kowski, J. Kukielski, P. Bauk and M. Lenczewska, Z. Naturforsch. 35a (1980) 466.
- [14] H. Görner, J. Photochem. 13 (1980) 269; H. Gruen and H. Görner, Z. Naturforsch. 38a (1983) 928.
- [15] R. Lapouyade, K. Czeschka, W. Majenz, W. Rettig, E. Gilabert and C. Rullière, J. Phys. Chem. 96 (1992) 9643.
- [16] E.M. Gibson, A.C. Jones, A.G. Taylor, W.G. Bouwman, D. Phillips and J. Sandell, J. Phys. Chem. 92 (1988) 5449.
- [17] L.W. Peng, M. Dantus, A.H. Zewail, K. Kemnitz, J.M. Hicks and K.B. Eisenthal, J. Phys. Chem. 91 (1987) 6162.
- [18] Q. Shang and E.R. Bernstein, J. Chem. Phys. 97 (1992) 60.
- [19] O. Kajimoto, K. Yamasaki and K. Honma, Faraday Discussions Chem. Soc. 85 (1988) 65.
- [20] R. Howell, D. Phillips, H. Petek and K. Yoshihara, Chem. Phys. 188 (1994) 303.
- [21] C. Dedonder-Lardeux, C. Jouvet, S. Martrenchard, D. Solgadi, J. McCombie, B.D. Howells, T.F. Palmer, A. Subaric-Leitis, C. Monte, W. Rettig and P. Zimmermann, Chem. Phys. 191 (1995) 271.
- [22] A. Safarzadeh-Amiri, J. Photochem. Photobiol. A 43 (1988) 43.
- [23] L.H. Spangler, R. Zee and T.S. Zwier, J. Phys. Chem. 91 (1987) 2782.

- [24] T. Suzuki, N. Mikami and M. Ito, *J. Phys. Chem.* 93 (1989) 5124.
- [25] T. Urano, M. Maegawa, K. Yamanouchi and S Tsuchiya, *J. Phys. Chem.* 89 (1989) 3459.
- [26] W.-Y. Chiang and J. Laane, *J. Chem. Phys.* 100 (1994) 8775.
- [27] T. Hansson, R. Daum, R. Nörenberg and J. Schroeder, unpublished results.
- [28] S.S. Siewert and L.H. Spangler, *J. Phys. Chem.* 99 (1995) 9316.
- [29] S. Yan and L.H. Spangler, *J. Phys. Chem.* 99 (1995) 3047.
- [30] V.H. Grassian, J.A. Warren and E.R. Bernstein, *J. Chem. Phys.* 90 (1989) 3994.
- [31] J.S. Baskin, D. Semmes and A.H. Zewail, *J. Chem. Phys.* 85 (1986) 7490; J.S. Baskin, P.M. Felker and A.H. Zewail, *Chem. Phys.* 86 (1987) 2460, 2483.
- [32] P.M. Felker and A.H. Zewail, in: *Femtosecond chemistry*, eds. J. Manz and L. Wöste, Vol. I (VCH Publishers, Weinheim, 1995) ch. 5.
- [33] T. Ueda and T. Shirmanouchi, *J. Mol. Spectry.* 28 (1968) 350.
- [34] B.W. Keelan and A.H. Zewail, *J. Phys. Chem.* 89 (1985) 4939.
- [35] MOPAC-6, QCPE, Bloomington, IN, USA.
- [36] W. Rettig, B. Strehmel and W. Majenz, *Chem. Phys. Letters* 173 (1993) 525.
- [37] T. Beyer and D.F. Swinehart, *Comm. Assoc. Comp. Mach.* 16 (1973) 379.
- [38] F. Negri and G. Orlandi, *J. Phys. Chem.* 95 (1991) 748.