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Vries, Harmen de; Wiersma, Douwe A.

*Published in:*  
Physical Review Letters

*DOI:*  
[10.1103/PhysRevLett.36.91](https://doi.org/10.1103/PhysRevLett.36.91)

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*Document Version*  
Publisher's PDF, also known as Version of record

*Publication date:*  
1976

[Link to publication in University of Groningen/UMCG research database](#)

*Citation for published version (APA):*

Vries, H. D., & Wiersma, D. A. (1976). Homogeneous Broadening of Optical Transitions in Organic Mixed Crystals. *Physical Review Letters*, 36(2), 91-94. <https://doi.org/10.1103/PhysRevLett.36.91>

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periment by bombarding, e.g.,  $^{107}\text{Ag}$  or  $^{208}\text{Pb}$  with  $^{16}\text{O}$  in small steps of incident energy (about 50 MeV/nucleon) from 0.05 to 2.1 GeV/nucleon (if possible higher) and systematically measuring the shock angles.<sup>12</sup> These measurements will enable us to explore the energy function  $W(\rho, T)$ , its eventual isomer structures, and also the temperature behavior of a highly compressed nuclear gas. Such experiments should presently be possible without major difficulties.

We thank Professor E. Schopper for many valuable discussions.

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\*Work supported by Bundesministerium für Forschung und Technologie and by Gesellschaft für Schwerionenforschung.

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<sup>10</sup>A recalibration of the data of Ref. 8 has shifted the experimental Mach angles to somewhat larger values as shown in Table I (E. Schopper, private communication).

<sup>11</sup>The occurrence of transparency—as postulated by M. I. Sobel, P. J. Siemens, J. P. Bondorf, and H. A. Bethe, to be published—can presently not be ruled out.

<sup>12</sup>The strength of the density isomer may depend on the number of nucleons. This can be experimentally found out by systematically choosing heavier projectile and target nuclei and repeating the excitation function of the Mach angle.

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## Homogeneous Broadening of Optical Transitions in Organic Mixed Crystals

Harmen de Vries and Douwe A. Wiersma

*Laboratory for Physical Chemistry, University of Groningen, Zernikelaan, Paddepoel, Groningen, The Netherlands*

(Received 21 October 1975)

We have used the phenomenon of laser-induced molecular photodissociation to determine the homogeneous linewidth at 2 K of the origin (zero-phonon line) and a vibronic transition in the mixed-crystal absorption spectrum of dimethyl *s*-tetrazine in durene. From the measured 55-MHz (upper limit) homogeneous width of the origin we conclude that in the vibrationless excited state coherence persists at least during the 6-nsec lifetime. The 29-GHz homogeneous vibronic linewidth is ascribed to vibrational relaxation.

It is still mainly a matter of speculation as to what extent the linewidths in the low-temperature "sharp" line absorption and emission spectra of organic mixed crystals are inhomogeneously broadened.<sup>1</sup> In organic crystals the only report of a homogeneous linewidth of a vibrationless transition comes from Hochstrasser and Li<sup>2</sup> who showed that the origin (zero-phonon line) of the lowest singlet state in azulene as guest in naphthalene was mainly homogeneously broadened. In this exceptional case there is an extremely fast (2.6-psec) nonradiative electronic relaxation process that is responsible for the observed 2-cm<sup>-1</sup> origin linewidth. Recently Marchetti, McCoglin, and Eberly<sup>3</sup> reported a measurement of

the homogeneous linewidth of a vibronic transition in the spectrum of pentacene embedded in a *p*-terphenyl host crystal. The underlying homogeneous linewidth of the 3-cm<sup>-1</sup>-wide vibronic transition was found to be 0.026 cm<sup>-1</sup> and the authors concluded from this that vibrational relaxation in this state was as slow as 200 psec. The question of course arises whether such a slow vibrational relaxation process is typical for organics at low temperature or that again an exceptional case was studied. We have designed an optical "hole-burning" experiment that not only answers this latter question, but also permits us, for the first time, to measure directly the underlying homogeneous linewidth of a zero-phonon

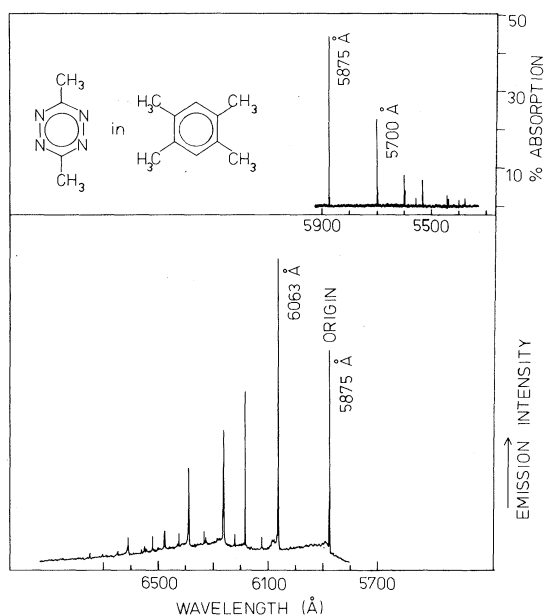


FIG. 1. The absorption and laser-induced (at 5700 Å) emission spectra of DMST in durene at 2 K. The intensity distribution in emission is not realistic because of inevitable decomposition of DMST during excitation.

line in an organic mixed crystal. Related (low-resolution) hole-burning observations on solid solutions of organic molecules were recently reported by Kharlamov, Personov, and Bykovskaya and by Gorokhovskii, Kaarli, and Rebone.<sup>4</sup>

In this note we report results of a homogeneous-linewidth study at 2 K on some selected optical transitions in the spectrum of dimethyl *s*-tetrazine (DMST) as guest in a durene host lattice. The most interesting property, for our purposes, of DMST is that it photodecomposes. In fact Meyling, van der Werf, and Wiersma<sup>5</sup> recently showed the quantum yield of photodissociation for this molecule in the gas phase to be close to 1, while a 6-nsec excited-state lifetime was also reported. We have studied the low-temperature laser-induced photodecomposition of DMST in a durene host crystal while exciting several (presumably) inhomogeneously broadened transitions in the absorption spectrum of DMST. Figure 1 shows the absorption and emission spectra of DMST in durene at 2 K in the region of the lowest singlet state of DMST.<sup>6</sup> The origin (zero-phonon line) of the absorption system is found at 5875 Å. Figure 2 shows that under high optical resolution this absorption line is found to be a 0.25-cm<sup>-1</sup>-wide Gaussian-shaped line, which supports our speculation that this line is inhomoge-

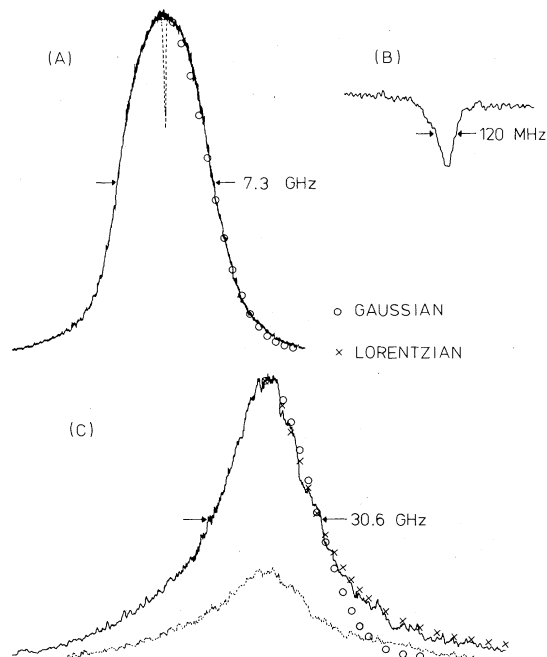


FIG. 2. cw-dye-laser-induced excitation (absorption) spectra of (a) the origin at 5875 Å and (c) the vibronic transition at 5700 Å of DMST in durene at 2 K. The cw dye laser was slowly scanned (20 MHz/sec) through the absorption regions with instantaneous bandwidth ( $\sim$  resolution) of  $\leq 20$  MHz. The dotted spectra were obtained after 1 sec laser burning (effective bandwidth 30 MHz) in the origin and 5 min burning (effective bandwidth 100 MHz) in the vibronic line (at the top). (b) High-resolution scan of the hole burned in the zero-phonon line.

neously broadened. The next (vibronic) line in the absorption spectrum is located at 5700 Å and, to our surprise, we found, see also Fig. 2, this line very close to being Lorentzian shaped with a 1-cm<sup>-1</sup> linewidth. This of course suggests that this line is homogeneously broadened and this is indeed confirmed by our laser-induced photodissociation experiments that will be discussed now. In these experiments a narrow-band cw dye laser is tuned to, e.g., the zero-phonon line in the absorption spectrum of DMST at 5875 Å. If this transition is indeed inhomogeneously broadened, we expect only those molecules to be excited and subsequently to decompose that are situated at lattice sites whose central frequencies are within a homogeneous linewidth ( $\Delta\nu_h$ ) of the exciting laser frequency.<sup>7</sup> Thus the laser initially will burn a persistent "hole" of width (roughly)  $2\Delta\nu_h$  in this absorption line that can be probed afterwards. The results of such hole-burning experi-

ments on the 5700- and 5875-Å absorption bands of DMST are shown in Fig. 2. The figure shows that the laser indeed burns a hole in the zero-phonon line but not in the vibronic line. This confirms the suggestion, made earlier on the basis of line-shape considerations, that the origin is inhomogeneously broadened, but the vibronic transition mainly homogeneously broadened. The hole burned in the zero-phonon line was found to be persistent at 2 K throughout the time of the experiment (~4 h).

The absorption bands of DMST in durene shown in Fig. 2 were obtained as follows. A single-mode cw dye laser using Rhodamine 6G was slowly scanned (20 MHz/sec) through the absorption region, while the band at 6063 Å in the emission spectrum was photoelectrically detected using a ½-m Jarrel-Ash monochromator. The sensitivity of this excitation technique in monitoring weak absorptions is clearly demonstrated by the fact that naturally abundant isotopic species of DMST, present in the crystal with an estimated optical density of  $\approx 0.02$ , could be detected easily and studied. While the actual hole-burning experiments were done using circa 100 mW of cw dye-laser power, the absorption probe beam was only 0.2% of this intensity. The laser output in all experiments was studied on an oscilloscope via a scanning Fabry-Perot interferometer.

Figure 2 also shows a high-resolution tracing of the hole burned in the zero-phonon line from which its width is measured to be  $120 \pm 20$  MHz. The effective (Gaussian) linewidth of the cw dye laser over the hole-burning time of 1 sec is 30 MHz, and if this is taken into account the homogeneous linewidth of the zero-phonon transition is calculated to be  $55 \pm 10$  MHz. This certainly represents an upper limit considering the fact that the unknown, but certainly less than 20 MHz, laser frequency jitter during the actual probing is not taken into account. In general the homogeneous linewidth (full width at half-maximum)  $(\pi T_2)^{-1}$  of any absorption line is determined by<sup>8</sup>  $1/T_2 = 1/T_2^* + 1/2T_1$  where  $T_1$  is the longitudinal and  $T_2$  the transverse relaxation time in the optical analog of the Bloch equations.<sup>9</sup> In DMST the lifetime-broadening ( $T_1$ -effect) contribution to the homogeneous linewidth is calculated to be 25 MHz. The maximum contribution of phase-destructive events ( $T_2^*$  effects) to the homogeneous linewidth of the vibrationless transition in DMST in thus calculated to be 30 MHz. This is an important result because it shows, for the first time, the magnitude of the low-temperature con-

tribution of electron-phonon coupling to the homogeneous linewidth of organic-mixed-crystal absorptions. It also suggests the interesting possibility of performing, on a nanosecond time scale, photon-echo measurements<sup>10</sup> on molecular crystals.<sup>11</sup>

On prolonged laser irradiation of the zero-phonon line the hole not only deepens but also significantly widens. This interesting effect is presently being studied in greater detail. It is also of interest to note that in our (photodissociation) hole-burning experiments the time-integrated photon flux plays the same role as the instantaneous photon flux in the usual (population) hole-burning experiments.<sup>12</sup> Figure 2 further shows that the 5700-Å absorption line, on laser irradiation, disappears as a whole. We conclude that the 30.6-GHz linewidth of this vibronic transition is mainly homogeneous. Assuming the underlying inhomogeneous linewidth to be the same as that of the origin (7.3 GHz), we calculate from a Voigt line-shape analysis<sup>13</sup> a true homogeneous width of 28.8 GHz. We conclude that the vibrationally excited-state lifetime ( $T_1$  process) of this level is only 5.5 psec and we attribute this to vibrational relaxation. Marchetti, McColgin, and Eberly<sup>3</sup> measured for the first vibronic state of pentacene a lifetime of at least 200 psec, which implies that vibrational relaxation processes (and thus electron-phonon coupling processes) vary widely in organic mixed crystals. Obviously much more work needs to be done in this area to understand these variations.

Finally we demonstrate how narrow-band laser-induced emission can be used to measure vibrational relaxation in the ground state of DMST. Figure 3 shows, under high optical resolution ( $0.1 \text{ cm}^{-1}$ ), the 5875- and 6063-Å emission lines of DMST in durene, while exciting with a cw dye laser the (vibronic) 5700-Å absorption of DMST. The origin emission line shape and width are found to be identical to what is observed in absorption. The emission to the vibrationally excited ground state however is found to be a Lorentzian line with 37.0-GHz linewidth. We interpret this as a homogeneous width caused by vibrational relaxation in the ground state. Assuming the underlying inhomogeneous linewidth to be identical to that of the pure electronic transition, we find a true homogeneous linewidth of 35.4 GHz, from which a ground-state vibrational relaxation time of 4.5 psec is calculated. Incidentally one should note that the 5700-Å absorption and 6063-Å emission lines of DMST correspond

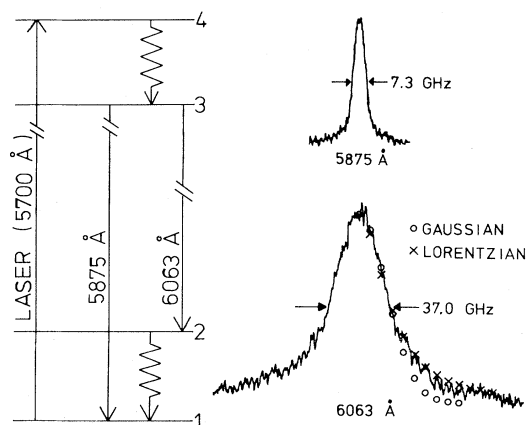


FIG. 3. High-resolution ( $0.1 \text{ cm}^{-1}$ ) cw dye-laser-induced emission spectra of the zero-phonon line at  $5875 \text{ \AA}$  and vibrational transition at  $6063 \text{ \AA}$  of DMST in durene at 2 K after excitation of the vibronic transition at  $5700 \text{ \AA}$ . In the excitation-emission scheme of DMST the numbers 1-4 have the following meaning: 1 stands for ground state, 2 for vibrationally excited ground state, 3 for vibrationless excited state, and 4 for vibronic state. The wavy arrows indicate nonradiative processes ( $T_1$  effects) that may deplete levels 2 and 4.

to excitation of the same mode in the excited and ground states, respectively, and our experiments thus show the relaxation times of these states to be remarkably similar.

Concluding we would say that our experiments imply that any photoinduced process such as dissociation, ionization, or isomerization can be used to study homogeneous-linewidth effects in organic mixed crystals. It further seems that the prospects of utilizing cw dye lasers in the study of relaxation times in excited states of organic crystals are very promising indeed.

The investigations were supported by the Netherlands Foundation for Chemical Research (S.O.N.) with financial aid from the Netherlands

Organization for the Advancement of Pure Research (Z.W.O.).

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<sup>6</sup>J. H. Meyling and D. A. Wiersma, unpublished. The concentration of DMST in durene is estimated to be  $10^{-3}$  mol %. Polarization studies on the lowest singlet state of DMST in durene show this state to be, as expected (Ref. 5), a  $B_{3u} \pi\pi^*$  state. The absorption and emission spectra of DMST in durene are at present being studied in greater detail and will be reported elsewhere.

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<sup>8</sup>See, e.g., A. C. G. Mitchell and M. W. Zemansky, *Resonance Radiation and Excited Atoms* (Cambridge Univ. Press, London, England, 1934).

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