Volume Change Associated with Large Photoinduced Dipole Formation in a Rigid Donor−Acceptor Compound: New Approach to Optoacoustic Volume Determination

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Received: June 23, 1998; In Final Form: August 12, 1998

Time-resolved laser-induced optoacoustic spectroscopy was used to study the charge separation process taking place in the excited state of a donor−bridge−acceptor (D-br-A) compound in alkane solvents. This molecule contains a D−A pair separated by a rigid saturated hydrocarbon bridge 6 sigma bonds long. Excitation at 308 nm results in very efficient long-range charge separation, leading to formation of a charge-transfer (CT) state with a dipole moment of 38 D. By monitoring the pressure waves generated during the decay of the excited species, we could discern three consecutive relaxation processes. To separate the contributions of enthalpy and structural volume changes (ΔV_{str}), experiments were carried out with a series of *n*-alkanes having different photothermal properties. However, the usual separation method clearly failed for this system, and a new approach was developed to ensure that ΔV_{str} remained constant across the alkane series. This consisted of selecting conditions where the solvent compressibility could be considered constant over the experimental range. In this way, ΔV_{str} values between −110 and −200 mL/mol were obtained, depending on alkane length and temperature. These are remarkably large contractions, which can be attributed only to electrostriction of the alkane solvent around the dipolar CT species. Interestingly, the contractions are as large as predicted by classical electrostatic theory. The quantum yield of triplet formation, Φ_T, determined from the optoacoustic data, revealed a strong dependence on the oxygen content of the solution. A value of $\Phi_T = 0.04$ was obtained for the intrinsic quantum yield in the absence of oxygen.

1. Introduction

The study of reaction volume changes occurring during electron transfer reactions is of interest with respect to two main topics: Intrinsic molecular volume changes in a donor−acceptor (D−A) system may yield information on the electron transfer mechanism, whereas volume changes from expansion or contraction of the solvent shells around the D−A compound might give valuable insight into the thermodynamics of the solvent reorganization processes.

By means of laser-induced optoacoustic spectroscopy (LIOAS), one can monitor structural volume changes (ΔV_{str}) in addition to the volume changes caused by heat release processes taking place after excitation of a chromophore.[1,2] With this method, the pressure waves generated by the relaxation of the absorbing species are detected by a piezoelectric transducer. Consecutive decay processes with distinct time constants can be observed separately, yielding time-resolved information.[3]

Earlier we showed that for D-br-A compound **1** in *n*-alkanes, a contraction of ∼40 mL/mol occurs upon electron transfer and subsequent exciplex formation (see Figure 1).[4] By taking into account simple electrostatic considerations, we estimated that the contribution of solvent reorganization should be around −15 mL/mol, leaving an intrinsic molecular volume change of −25 mL/mol. The latter contribution could be attributed to the exciplex formation taking place in this molecule, where the distance between D and A (R_{DA}) is reduced from 5.4 Å in the ground state to ∼3−3.5 Å in the exciplex state, leading to the smaller volume.[5] Indeed, as subsequently pointed out by Schmidt and Schütz,[6] such a contraction upon exciplex formation is in line with the contact−complex theory of Yoshimura and Nakahara.[7]

To put these interpretations further to the test, we decided to study the solvent volume changes separately. For a suitable probe molecule we selected D-br-A compound **2**, which contains a dimethoxynaphthalene group as a donor and a dicyanovinyl moiety as acceptor, separated by a norbornyl-like hydrocarbon bridge with an effective length of 6 sigma bonds, or a center-to-center separation of 9 Å. Upon excitation at 308 nm in alkane solution, fast charge separation takes place with a quantum yield of unity, resulting in a so-called "giant dipole" charge-transfer (CT) state ($\mu = 38$ D) with a lifetime of 40 ns.[8] This rather long lifetime offers the possibility of distinguishing the decay of the CT state from that of the initially excited local dimethoxynaphthalene state with the LIOAS technique. Since this rigid compound cannot undergo significant conformational changes, any volume change observed should be attributable to the interaction with the solvent. Moreover, in alkanes no specific interactions are to be expected,[9] and only a general response related to solvent electrostriction could take place.

A further advantage of this molecule pertains to its much larger dipole moment than **1**, which should result in a considerably larger solvent contraction. Indeed, our experiments clearly confirmed this hypothesis; however, they also showed that the magnitude of the contraction depends on the properties of the

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10.1021/jp982751h CCC: $15.00

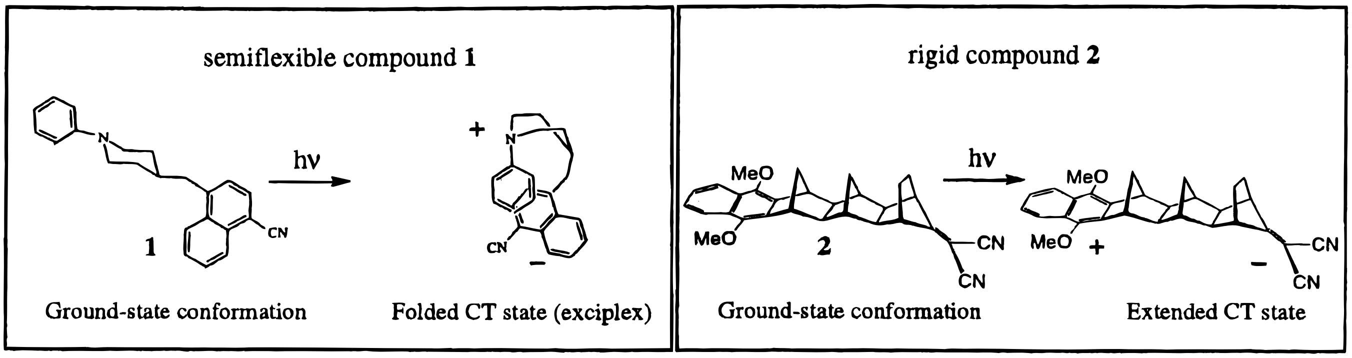

Figure 1. Structures of the D-br-A compounds **1** and **2** in ground and CT state. The semiflexible bridge of **1** allows for molecular folding in the charge-separated D^+-br-A^- state to form the exciplex (with an R_{DA} of 3−3.5 Å), whereas **2** incorporates a rigid bridge that keeps D and A fixed at a center-to-center distance of 9 Å under all circumstances.

solvent itself. This posed a problem for obtaining accurate quantitative information on the volume change. Normally, the procedure for separating different contributions to the observed signal in organic solvents consists of using a series of *n*-alkanes, where the enthalpy and volume changes are supposed to be constant.[4,10] In this case, the alkane variation method clearly failed, given that ΔV_{str} was obviously not constant, and forced us to use a slightly different approach involving adjustment of the temperature of the various alkane solutions to control the compressibility of the solvent. Although this new approach seems valid, it cannot be applied over a wide range of experimental values, this leading to a relatively large error. Nevertheless, some clear conclusions on the factors influencing the magnitude of the structural volume change could be drawn and could be given a consistent interpretation in terms of the simple dielectric continuum model. Furthermore, the relevance of the LIOAS results with respect to some other photophysical properties is discussed, leading to a value for the triplet quantum yield that agrees well with transient absorption results. Finally, the thermodynamics of CT state formation in **2** is briefly addressed, yielding an estimate of the large negative entropy of solvation at room temperature.

2. Experimental Section

2.1. Materials. The synthesis of **2** has been published previously.[11] For a calorimetric reference compound we used 2-hydroxybenzophenone (2HOBP),[1] which was obtained from Merck and recrystallized from ethanol. The alkane solvents used (*n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, and *n*-dodecane) were purified before use by distillation or column chromatography.

2.2. Methods. The LIOAS setup consists of an FL2000 Lambda Physik-EMG 101 MSC excimer laser (XeCl, 308 nm) operating at 1 Hz, irradiating a 1-cm path length absorption cuvette equipped with a β-polyvinylidene difluoride film (40 μm thick) as a piezoelectric detector pressed against the cuvette wall parallel to the direction of propagation of the pump pulse. The signals were amplified 100 times (Comlinear E103) and fed into a transient recorder (Tektronix TDS 684A) operating at 1 gigasample/s and averaging 200 signals.

The absorbance of the reference solution at 308 nm (measured with a Shimadzu UV-2102PC spectrophotometer) was matched within 2% to that of the sample solution (measured before and after the LIOAS experiment); the mean energy of the incident laser light (measured with a Laser Precision Corp. RJP735 head connected to an RJ7100 meter) was also kept similar for sample and reference. The laser beam was shaped by a 0.2-mm-wide slit in front of the cuvette. The solutions of **2** were deoxygenated by bubbling with solvent-saturated Ar for 15−20 min.

2.3. Signal Handling. The sample signal was treated as a convolution of the instrument response function (given by the reference compound, which releases all of the excitation energy as heat within 1 ns) and a time-dependent pressure evolution function associated with the relaxation of the excited species. With the help of a deconvolution program (Sound Analysis version 1.13, Quantum Northwest) the lifetime (τ_i) and amplitude (φ_i) values were obtained for the various decay processes. For a process with a quantum yield of unity, the amplitude is given by eq 1:[9,12]

$$\varphi_i = \frac{q_i}{E_\lambda} + \frac{\Delta V_{str}}{E_\lambda}\left(\frac{c_p\rho}{\beta}\right) \tag{1}$$

where q_i is the heat released, E_λ the laser excitation energy, β the cubic expansion coefficient, c_p the heat capacity, and ρ the density. A plot of φ_i versus the solvent thermoelastic parameters ratio ($c_p\rho/\beta$) will yield q_i from the intercept (corresponding to ΔH_i, the enthalpy change of the process) and ΔV_{str} from the slope, assuming that both the heat release and volume change remain constant when $c_p\rho/\beta$ is varied.

To minimize differences in arrival time of the pressure waves due to the temperature dependence of the sound velocity in fluids, we thermostated the cuvette with an accuracy of 0.1 K. Still, when working with heated or cooled solutions, the long-term variation in temperature between sample and reference could be as large as 0.5 K, leading to differences in arrival time as great as 10 ns. This meant that the deconvolution program sometimes had difficulties in finding the correct time-shift between reference and sample signal and ended up in a local minimum, which introduces an error in the relative magnitudes of the first and second amplitude. Worse still, a slight change of temperature during one measurement results in an ill-defined arrival time (i.e., a "smearing" of the signal), in which case no true minimum can be found anymore and the measurement should be rejected. For these reasons, the signal was fitted over a wide shift range in steps of 1 ns, and the resulting χ^2 values were plotted as a function of the time-shift. In this way, we obtained a good impression of the various minima which provided more-reliable values for the respective amplitudes as well as a good estimate of the error limits of the particular measurement.

3. Results and Discussion

3.1. LIOAS Measurements of 2 in *n*-Alkanes. LIOAS signals of **2** in various alkane solvents (*n*-hexane, *n*-heptane,

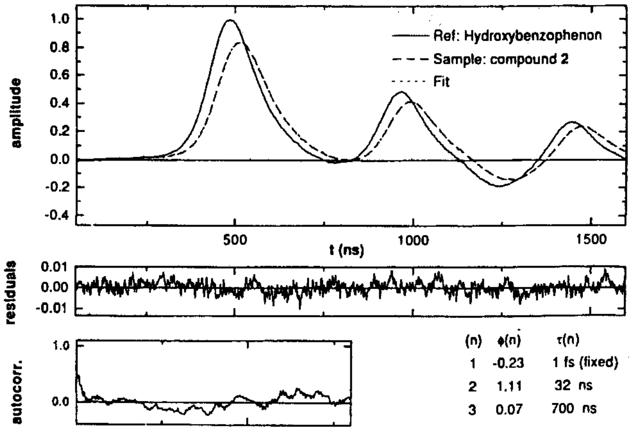

Figure 2. LIOAS signals of sample (**2**) and reference (2HOBP) in *n*-heptane at room temperature together with the fitted curve, residuals, and autocorrelation function. Note that the fit completely coincides with the measured sample signal. The fit parameters obtained by the deconvolution procedure for this particular measurement are also shown.

n-octane, *n*-nonane, *n*-decane, and *n*-dodecane) were obtained as described above. At least three fresh sample solutions were prepared for each solvent, and a set of 3 or 4 signals (each averaged 200 times) was measured for every sample. A typical LIOAS signal of **2** in *n*-heptane at 20 °C is shown in Figure 2, together with that of the calorimetric reference compound 2HOBP. Since transient processes are occurring in the excited state of **2** within the experimental time-window of the LIOAS experiment, we analyzed the signals by using a deconvolution procedure (see *Experimental Section*).

Satisfactory fits could be obtained with three consecutive decay constants. The first of these (τ_1) had a value of <1 ns, shorter than the time resolution of the experiment. However, the associated amplitude (φ_1) could be obtained reliably and was hardly influenced by the value of the lifetime used for the fit. In practice, τ_1 was simply fixed to a value between 1 fs and 1 ns, and the 5 other parameters were left free in the fitting routine. With our knowledge of the photophysical behavior of **2**, we can readily attribute τ_1 and φ_1 to the decay process from the Franck−Condon excited state to the relaxed S_1 state plus the decay of the S_1 state to the CT state via electron transfer, since these processes take place on a picosecond time scale. Therefore, this first amplitude essentially contains all the information required for determining the enthalpy and volume change upon CT state formation.

The second decay time amounted to 25−35 ns in every case, depending on the extent of deoxygenating. A similar lifetime was found with time-resolved fluorescence studies for the emission of the CT state of **2** in *n*-hexane (40 ns),[8] enabling us to identify τ_2 and φ_2 with the decay of the CT state.

The third decay time was not always observed clearly but, when detectable, had a value of 500 ns to 2.5 μs, with a relatively small φ_3, 0.03−0.15. Less-efficient deoxygenating shortened the lifetime and increased the φ_3, which is discussed in detail in section 3.4. This decay can be assigned to a triplet state of **2** (^{3}D*-br-A), which is formed in low yield from the CT state. It is also observed in LIOAS measurements on a model compound of **2** that lacks the acceptor group, thus supporting the interpretation that the decay is due to a localized dimethoxynaphthalene state.[13] Transient absorption studies also gave clear indications for formation of this triplet state in **2**.[14]

Thus the kinetic information obtained with the LIOAS measurements agrees very well with that of optical experiments (see Figure 3 for a schematic representation of the three decay processes).

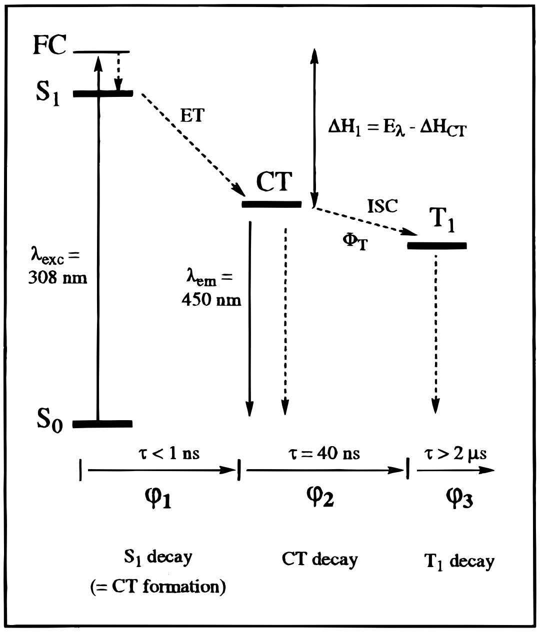

Figure 3. Photophysical processes taking place in photoexcited **2** in alkane solvents, together with the assignment of the observed LIOAS amplitudes φ_i to the various relaxation processes. Solid arrows represent optical transitions; dashed arrows represent dark processes that release heat. S_0 = ground state D-br-A, FC = locally excited Franck−Condon state (at 308 nm); S_1 = locally excited singlet dimethoxynaphthalene state ^{1}D*-br-A; CT = charge transfer state D$^+$-br-A$^-$; T_1 = locally excited triplet dimethoxynaphthalene state ^{3}D*-br-A; ET = electron transfer; and ISC = intersystem crossing.

TABLE 1: Experimental φ_1 Values, Solvent Thermoelastic Properties ($c_p\rho/\beta$), and Isothermal Compressibility (κ_T) Obtained from the Literature,[15] and Calculated ΔV_{str} Values (eq 1) for 2 in *n*-alkanes at Room Temperature (297 K)

n-alkane	$\varphi_1{}^a$	$c_p\rho/\beta$ (kJ/mL)	κ_T (10^{-9} Pa^{-1})	$\Delta V_{str}{}^b$ (mL/mol)
n-hexane	−0.25	1.07	1.70	−187
n-heptane	−0.22	1.22	1.44	−154
n-octane	−0.22	1.34	1.28	−140
n-nonane	−0.23	1.45	1.18	−132
n-decane	−0.20	1.53	1.09	−118
n-dodecane	−0.21	1.69	0.98	−109

[a] Experimental error is ±0.03. [b] The error is ±10 mL/mol, based on the error in φ_1.

3.2. Structural Volume Changes.

As indicated in Figure 3, the LIOAS amplitude φ_1 is associated with formation of the CT state in **2** and consists of a contribution from the heat released in going from the Franck−Condon excited state to the CT state (which results in an expansion of the solvent) and a contribution from the structural volume change ΔV_{str}. Surprisingly, this φ_1 is clearly negative in all *n*-alkanes studied, varying between −0.20 and −0.25 at room temperature (see Table 1).

Considering that the corresponding heat evolution $q_1 = E_\lambda - \Delta H_{CT}$ should cause an expansion, the observed negative amplitude indicates that a very large structural contraction takes place. A first approach to calculating ΔV_{str} from φ_1 can be made by using eq 1 if a value of the enthalpy of the CT state is known. An estimate of ΔH_{CT} based on the CT emission energy[8] of **2** in *n*-hexane (22 200 cm^{-1}) and correcting for the reorganization energy of ~4000 cm^{-1} yields 314 kJ/mol. However, we prefer to use the experimental value of ΔH_{CT} = 286 kJ/mol (as obtained below), which yields q_1 =102 kJ/mol. The contribution to the LIOAS amplitude solely from the heat release process is then $q_1/E_\lambda \approx 0.26$. Taking the experimental values of φ_1 for the various alkanes and using eq 1, we calculated ΔV_{str} to be on the order of -100 to -200 mL/mol (Table 1). This remarkable finding is in fact the main result of this study, irrespective of the fact that only an estimate of ΔH_{CT} was used for the calculation. The remainder of this section is dedicated to the analysis of the quantitative aspects of this enormous volume change.

Usually the contribution to φ_i from enthalpy and volume changes can be separated by plotting φ_i as a function of $c_p\rho/\beta$ (see section 2.3). However, in this case a meaningful plot could not be constructed; the φ_1 values in the various alkanes are all scattered around -0.22, showing no clear trend with $c_p\rho/\beta$. Moreover, a linear fit to these data points would yield a negative intercept, which would mean that the process is endothermic This obviously cannot be the case, in view of the large energy difference between the initially excited Franck–Condon state and the CT state as mentioned above.

This breakdown of the alkane variation method has been noted before, especially in cases where a highly dipolar species is involved.[4,16,17] This happens because ΔV_{str} is not constant across the alkane series (as is obvious from Table 1) but depends to a large extent on solvent properties. In terms of simple electrostatic theory, the solvent volume change is described by the electrostriction effect, i.e., the contraction of the solvent shells around ionic or dipolar species. For the dipolar case, the following expression has been derived:[4,18]

$$\Delta V_{\mathrm{el}} = -\left(\frac{\mu^2}{r^3}\right)\frac{(\epsilon + 2)(\epsilon - 1)}{(2\epsilon + 1)^2}\kappa_{\mathrm{T}} \qquad (2)$$

where ΔV_{el} represents the electrostriction volume change, μ is the dipole moment of the solute, r is its effective cavity radius, ϵ is the solvent dielectric constant, and κ_{T} is the isothermal compressibility of the solvent.

For a rigid compound such as **2**, the parameter μ^2/r^3 is constant over a whole range of solvents, and the solvent dielectric function $(\epsilon + 2)(\epsilon - 1)/(2\epsilon + 1)^2$ does not vary much either, but κ_{T} decreases considerably with increasing alkane chain length. In fact, with eq 2, ΔV_{el} is calculated to be 1.6 times higher in *n*-hexane than in *n*-dodecane. Since the observed volume change of compound **2** is unlikely to contain significant contributions other than solvent electrostriction (in contrast to the extra contraction occurring in **1** because of molecular folding),[4] ΔV_{str} may simply be equated to ΔV_{el}. This explains the problem encountered upon applying the alkane variation method to CT state formation in **2**: The φ_1 values in the shorter alkanes are lowered because of their larger negative ΔV_{el}, masking the expected correlation with $c_p\rho/\beta$.

To test the dependence of ΔV_{str} on κ_{T} as predicted by eq 2, we carried out temperature-dependent LIOAS measurements in *n*-heptane, since the solvent compressibility κ_{T} can be varied substantially by changing the temperature. This is shown in Figure 4, where the right-hand side of eq 2 [the expression $(\epsilon + 2)(\epsilon - 1)/(2\epsilon + 1)^2\ \kappa_{\mathrm{T}}$, hereafter referred to as the “solvent compressibility expression”] is plotted versus temperature for 4 alkanes.

Of course we should check now whether the other variables in eq 1 are affected by the variation in temperature, to avoid introducing errors attributable to changing properties of the solvent. For q_1 we expect only a slight variation with temperature, since the dielectric constant (the most important factor determining the solvation enthalpy) depends only weakly on temperature ($\mathrm{d}\epsilon/\mathrm{d}T = -0.0014$ for *n*-heptane). The variation of the thermoelastic parameters $c_p\rho/\beta$ was determined experimentally by measuring the reference signal at various temperatures. Although the intensity of the reference signal decreases significantly upon heating the solution (by 16%, range, 15–35 °C), this is not due to a change in $c_p\rho/\beta$. To understand this, consider that the total magnitude of any LIOAS signal depends also on κ_{T},[1,19] regardless of the origin of the signal. We stress that this effect does not interfere with our proposed method because the signal of **2** is affected in two ways by the change in compressibility: first through the structural volume change itself, and then through the “scaling” of the total signal with κ_{T}. After correcting for the change in κ_{T} with temperature, $c_p\rho/\beta$ appeared to remain constant within 1% over the range 15–35 °C, which is well within the experimental error. Thus, by varying the temperature, the compressibility is varied within one alkane, and therefore it is ΔV_{str} that is selectively varied, while ΔH and $c_p\rho/\beta$ are kept constant.

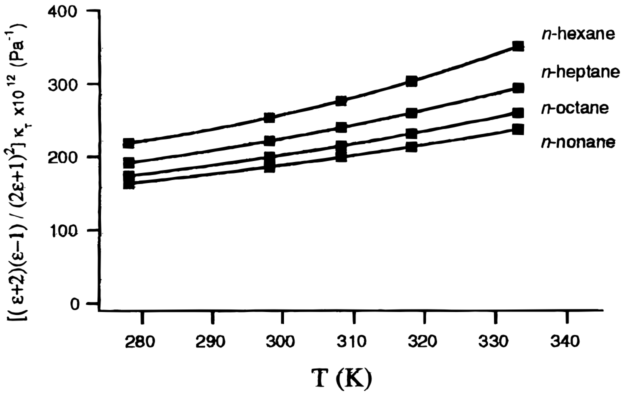

Figure 4. The solvent compressibility expression $(\epsilon + 2)(\epsilon - 1)/(2\epsilon + 1)^2\kappa_{\mathrm{T}}$ as a function of temperature for four different *n*-alkanes.

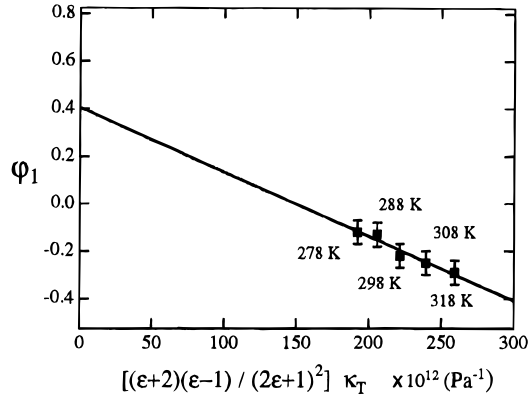

Figure 5. Temperature-dependent LIOAS experiment of **2** in *n*-heptane. The amplitude φ_1 is plotted versus the solvent compressibility expression (right side of eq 2).

Indeed, as shown in Figure 5, φ_1 becomes more negative upon increasing the temperature of a solution of **2** in *n*-heptane in the range 278–318 K. This is as expected, since at higher temperature κ_{T} is larger, leading to a larger solvent contraction. Using eq 2, a plot of φ_1 versus the solvent compressibility expression should yield ΔH_1 from the intercept and μ^2/r^3 from the slope (Figure 5). The latter amounts to ~860 kJ/mol, whereas the intercept gives $\Delta H_{\mathrm{CT}} = (230 \pm 35)$ kJ/mol. However, only a small range of values is achieved, and extrapolation to zero compressibility cannot be taken as a reliable value for the enthalpy content of the CT state. A major disadvantage of interpreting the data this way is that the resulting values rely numerically on the crude electrostatic model underlying eq 2. Furthermore, this analysis is applicable only to systems where the structural volume change arises solely from electrostriction.

Having shown a temperature effect on the value of ΔV_{str}, we can now use this finding to keep ΔV_{str} constant when the alkane

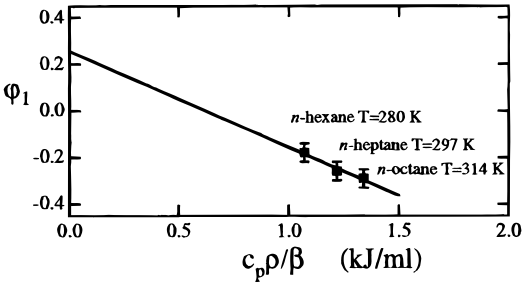

Figure 6. LIOAS amplitudes φ_1 of **2** in *n*-hexane ($T = 280$ K), *n*-heptane ($T = 297$ K) and *n*-octane ($T = 314$ K) as a function of $c_p\rho/\beta$. The temperatures were chosen in such a way that the solutions have equal values for the solvent compressibility expression.

is varied. Inspection of Figure 4 suggests that an experiment at "isocompressible" conditions may be carried out by selecting a horizontal cross-section at constant $(\epsilon + 2)(\epsilon - 1)/(2\epsilon + 1)^2 \kappa_T$, i.e., by adjusting the temperature of solutions of **2** in various alkanes in such a way that the solutions have matching values of the solvent compressibility expression. In this way, no assumptions regarding the expected volume change are necessary, and the basic procedure of the alkane variation method is not altered. Even if other factors (that do not depend on κ_T) do play a role in the magnitude of ΔV_{str}, this analysis still seems valid, since the properties of the alkanes are generally expected to become more similar to each other by this particular tuning of the temperature (i.e., heating the longer alkane *n*-octane and cooling the shorter *n*-hexane), resulting in a more-constant volume change.

Figure 6 shows such an isocompressibility plot for three alkanes at three different temperatures, where $[(\epsilon + 2)(\epsilon - 1)/(2\epsilon + 1)^2 \kappa_T]$ is constant at 2.2×10^{-10} Pa^{-1}. Again, the range of data is rather limited and the error large, but in this case a much more realistic intercept is found, affording $\Delta H_{CT} = (286 \pm 35)$ kJ/mol. While this value is obtained by extrapolation and might be fortuitously close to the value derived from emission studies, $\Delta G_{CT} = 314$ kJ/mol, the value of the slope is probably more reliable, especially considering that the estimated amplitude of the heat release contribution (~0.26) might also be taken into account as a data point at the intercept. Anyway, the slope of Figure 6 yields a value of $\Delta V_{str} = (-160 \pm 30)$ mL/mol, which represents the structural volume change of **2** in *n*-heptane at room temperature ($T = 24$ °C). Obviously, no general value for all alkanes can be given, since the volume change depends on the particular compressibility of the solvent.

A simple check commonly performed in LIOAS studies consists of analyzing the reverse volume change as well, which in the case of a cyclic process is expected to have the same magnitude (but with different sign) as the initial ΔV_{str}. This second structural volume change should contribute to φ_2, since the decay of the CT state of **2** is expected to be accompanied by a release of the electrostricted solvent molecules. However, as will be explained in section 3.4, the second amplitude is strongly influenced by residual oxygen quenching, which changes the branching ratio between internal conversion and intersystem crossing to such an extent that the value of φ_2 becomes dependent on oxygen concentration and cannot be used for determination of ΔV_{str}. On the other hand, the fact that φ_2 is always >1 for Ar-bubbled samples clearly confirms that a large positive contribution is present in addition to the expected heat release contribution of $\Delta H_{CT}/E_\lambda \approx 0.74$, which is thus in accord with the occurrence of a large positive structural volume change upon charge recombination.

In conclusion, the "isocompressibility" method seems to be the best way at present to evaluate our data to obtain an unbiased estimate of the structural volume change.

3.3. Magnitude of the Electrostriction Effect. With the observation of the huge structural volume change upon CT state formation in **2** in alkane solvents, the aim of testing the electrostriction effect has been fulfilled. Remarkably, although no large amplitude conformational changes are possible in either the ground state or the CT state of **2**, still, a much larger contraction is observed than for the semiflexible compound **1**. Thus, the effect of the greater dipole moment of the CT state of **2** than of **1** induces a much larger response from the surrounding solvent molecules. Furthermore, although the magnitude of the electric field exerted by the highly dipolar CT state of **2** is more or less constant across the alkane series (depending only slightly on the dielectric constant), the resulting electrostriction of the solvent molecules shows a clear trend with alkane chain length. This can be understood by considering that the same attraction force will have a much larger effect on a highly compressible solvent that consists of relatively light molecules, such as *n*-hexane, than on less-compressible solvents, such as the heavier alkanes.

In the case of a rigid D-br-A compound similar to **2** but with only 3 sigma bonds between D and A, the value of $\Delta V_{str} = -14$ mL/mol upon charge separation could be extracted from picosecond optical calorimetry experiments.[16] This appeared to agree well with the ΔV_{el} value calculated by means of eq 2, with 97 kJ/mol for μ^2/r^3 as derived from the solvent dependence of the CT emission band maximum. Unfortunately, for **2** no experimental value for μ^2/r^3 could be obtained, since the CT emission is clearly observed only in alkane solvents and no sufficient polarity range is achieved for a solvatochromic analysis. From time-resolved microwave conductivity studies, the dipole moment of the CT state of **2** is known to be 38 D,[8] which corresponds to transfer of a full electron across the D−A distance of 8 Å. Using an estimate of $r = 4.85$ Å for the cavity radius (obtained from modeling[20] the molecular volume of **2**) yields $\mu^2/r^3 = 760$ kJ/mol, which is comparable with the 860 kJ/mol resulting from the slope of Figure 5 (see section 3.2). Substituting $\mu^2/r^3 = 760$ kJ/mol in eq 2, we obtain $\Delta V_{el} = -167$ mL/mol for **2** in *n*-heptane at room temperature, which is indeed of the same order of magnitude as the experimental result [$\Delta V_{str} = (-160 \pm 30)$ mL/mol]. However, this estimate depends heavily on the "right" choice of *r*, and should only be taken as an indication that the huge volume change observed is not outside of the theoretically expected range. Alternatively, the CT state might be described as two separate monopoles, since the radical cation and anion are located at quite a large distance from each other. In that case, the electrostriction caused by both "ions" can be calculated as:[18]

$$\Delta V_{el} = -\left(\frac{e^2}{6R\epsilon^2}\right)(\epsilon + 2)(\epsilon - 1)\kappa_T \tag{3}$$

with *R* being the radius of the ion. For the two chromophores incorporated in **2**, an average value of $R = 4.5$ Å has been shown experimentally[11,16] to yield acceptable results. From the solvent properties of *n*-heptane at 24 °C, we obtained $\Delta V_{el} = -144$ mL/mol for the sum of the contractions caused by the charge-separated state of **2**. This is close to the experimental value of −160 mL/mol and also close to the outcome of the dipole treatment given above (−167 mL/mol), so the CT state of **2** apparently can be described either as two monopoles or as a single dipole.

Further evidence for the occurrence of large electrostriction volume changes in nonpolar solvents has been reported by Chen and Holroyd in studies on electron attachment reactions with organic compounds.[21] For instance, for the pyrimidine anion in trimethylpentane at 90 °C and 125 bar, they obtained a negative volume change of a similar magnitude (−188 mL/mol) as that for **2** in *n*-alkanes; their data also show a clear increase of the contraction with temperature. Electrostriction volumes were calculated by assuming that a glass shell of solvent molecules surrounds the ion and, although Chen and Holroyd maintain that these values are in better agreement with experiment than those obtained via formulas equivalent to eq 3, the glass-shell model itself does not show temperature-dependent behavior.

Summarizing, the present study has confirmed that not only ions can give rise to very large electrostriction effects, but also neutral molecules in which a giant dipole state can be (photo)-induced. Previously, eq 2 has been used to correct the LIOAS data of molecules with highly dipolar intermediates.[4,22] This seems now justified by the results with compound **2**, at least for alkane solvents.

3.4. Quantum Yield of Triplet Formation in 2. Apart from the determination of the ΔV_{str} described above, which formed the main incentive for this study, additional information regarding the photophysics of **2** can be extracted from the LIOAS data. Traditionally, LIOAS has often been used for measuring the triplet quantum yield (Φ_T) of organic compounds.[1] In time-resolved LIOAS experiments, Φ_T can be obtained in two ways: (1) directly from φ_3, which corresponds to the decay of the triplet state and is given by $\varphi_3 = \Phi_T (\Delta H_T/E_\lambda)$, with ΔH_T being the enthalpy content of the triplet state, or (2) from the sum of φ_1 and φ_2, taking into account the balance of energy in the system. In both cases, the neutral triplet state is assumed not to give rise to a significant volume change with respect to the ground state, and this was recently experimentally confirmed for the triplet state of two intramolecular CT compounds.[23] The formation of triplet states in water, however, can result in quite different volumes from those of the ground state because of changes in the specific solute-water hydrogen bond interactions.[9,24]

The total number of decay processes in **2** is 4 (see Figure 3), including fluorescence from the CT state, which has a quantum yield Φ_f of only 0.04 and a maximum at 450 nm ($E_f = 265$ kJ/mol) in alkanes,[8] corresponding to a contribution of $\varphi_f = \Phi_f (E_f/E_\lambda) = 0.025$. Obviously, the sum of the quantum yields for all processes should equal 1, since all excited molecules eventually return to the ground state and no net photochemistry occurs. Indeed, in many cases the deconvolution program yields a total amplitude ($\varphi_1 + \varphi_2 + \varphi_3$) of ~0.95−1.0, but for the triplet decay with its long lifetime, the recovered amplitude sometimes contains slight differences in baseline between sample and reference, leading to larger errors. Consequently, values of φ_3 in the range of 0.03−0.15 have been found, from which a value of Φ_T in the range 0.05−0.23 was calculated.

The sum $\varphi_1 + \varphi_2$ can be obtained much more accurately than φ_3 because of their short associated lifetimes (and without the errors attributable to separation of the two terms). A more reliable value for φ_3 can thus be determined by subtracting from 1.0 the value for $\varphi_1 + \varphi_2 + \varphi_f$. However, the range of φ_3 obtained in this way is still rather wide, between 0.03 and 0.1. Interestingly, closer inspection of the data shows a clear correlation between the lifetimes τ_2 and τ_3 and the magnitude of φ_3 [obtained via either (1) or (2)], i.e., both lifetimes get shorter in the presence of oxygen, with a concomitant increase of φ_3. Since the shortening of the CT and triplet-state lifetimes can be attributed to oxygen quenching, the increase in φ_3 must also be due to the presence of oxygen. Considering that the amount of heat released by quenching the triplet state with oxygen does not depend on the time scale in which it is released, we are forced to conclude that the quantum yield of triplet formation is increased by the presence of oxygen. In that case, it is the quenching of the CT state by oxygen that results in formation of the triplet state. Indeed, such oxygen-induced intersystem crossing has been observed before.[25] In our case, in the presence of oxygen, the lifetimes τ_2 and τ_3 ultimately decreased to 13.8 ns (from 32 ns) and to 118 ns (from 2.4 μs), respectively, whereas φ_3 underwent an almost 10-fold increase from 0.03 to 0.27!

From these data we obtained estimates of the quenching constants, using the lifetime of the triplet state as a measure for the concentration of oxygen in the solution. The triplet quenching constant was calculated to be 6×10^9 M^{-1} s^{-1}. The intersystem crossing (isc) rate can be written as $k_{isc} = k_{int} + k_{oxy} [O_2]$, where k_{int} is the intrinsic intersystem crossing rate in the absence of oxygen, and k_{oxy} is the oxygen-induced rate constant. Extrapolation of data with air to zero oxygen concentration leads to an estimate of $k_{int} = 1 \times 10^6$ s^{-1} and $k_{oxy} = 2 \times 10^{10}$ M^{-1} s^{-1}. The intrinsic triplet quantum yield, given simply by $\Phi_T = k_{int}\,\tau_{CT} = 0.04$, is lower than any of the values we obtained from the experimental data. Furthermore, this value is similar to values of Φ_T determined by transient absorption spectroscopy of **2** in benzene and dioxane (0.01 and 0.03, respectively)[14] under oxygen-free conditions for thoroughly evacuated samples, which supports the validity of our method of correcting Φ_T for the remnant oxygen concentration.

These findings contain a clear warning for obtaining triplet yields with the LIOAS method. Since the samples are usually only flushed with Ar or N_2, the removal of oxygen is far from efficient (especially in organic solvents) and may also vary considerably from one sample to another. When oxygen plays an active role in the photophysics of the molecule (as with **2**), erroneous and irreproducible results might thus be obtained. Failure to get consistent values of Φ_T for D-br-A compounds might be largely the result of this effect. In a wider context, when measuring and interpreting quantum yields and lifetimes, one should keep in mind that not only the decay of excited states is accelerated by oxygen (which is common knowledge), but also the branching ratio between photophysical pathways can be dramatically changed by the interaction.[25]

3.5. Thermodynamics of CT State Formation in 2. Finally, a short discussion regarding the thermodynamics of compound **2** in alkanes is of interest. A few attempts to disentangle ΔH_{CT} and ΔS_{CT} contributions to ΔG_{CT} via the relationship $\Delta G = \Delta H - T\Delta S$ with the help of LIOAS or optical calorimetry measurements (or both) have been reported for CT systems.[16,22] Unfortunately, the errors in ΔH_{CT} (from optoacoustic measurements) and ΔG_{CT} (calculated from emission data) are usually too large to allow calculation of a reliable value for their difference ($T\Delta S_{CT}$); the present study is no exception. However, ΔS_{sol} (the solvation entropy, ~ΔS_{CT}, see above) can be estimated in two ways, both based on the continuum model. First, using the experimentally obtained value of ΔV_{str} (= ΔV_{sol}), the following Maxwell relationship may be used:[16,21]

$$\Delta S_{sol} = \left(\frac{\beta}{\kappa_T}\right)\Delta V_{sol} \tag{4}$$

For **2** in *n*-heptane ($\Delta V_{str} \approx -160$ mL/mol), eq 4 yields $\Delta S_{sol} = -130$ J/mol K.

The second method is to write the entropy change upon solvation of a point dipole as the derivative of $\Delta G_{\rm sol}$ with respect to temperature, which leads to eq 5:[16,26]

$$\Delta S_{\rm sol} = -3\left(\frac{\mu^2}{r^3}\right)\frac{(d\epsilon^{-1}/dT)}{(2+\epsilon^{-1})^2} \qquad (5)$$

Using the same values for μ (38 D) and r (4.85 Å) as in section 3.3, we calculate $\Delta S_{\rm sol} = -131$ J/mol K. Thus, consistent values for the solvation entropy change are found within the continuum model. Again, these are large numbers (as expected, a factor of 10 greater than obtained for the compounds with the smaller excited-state dipole moments),[16,22] representing a substantial part of the free energy. For instance, at room temperature in *n*-heptane, $T\Delta S_{\rm sol}$ amounts to -38 kJ/mol, which implies that $\Delta G_{\rm CT}$ is significantly larger than $\Delta H_{\rm CT}$. Taking the estimates derived from the LIOAS experiments of $\Delta H_{\rm CT} = 286$ kJ/mol and $\Delta S_{\rm CT} = -130$ J/mol K, we obtain $\Delta G_{\rm CT} = 324$ kJ/mol. The $\Delta G_{\rm CT}$ estimated from the emission wavelength (correcting for the reorganization energy) amounts to 314 kJ/mol, which is surprisingly similar. Inasfar as the value of $\Delta H_{\rm CT}$ can be trusted, this coincidence of the $\Delta G_{\rm CT}$ values implies that the solvation entropy indeed plays a large role in the driving force of CT state formation for **2** in nonpolar solvents at ambient temperatures.

4. Conclusions

From time-resolved LIOAS experiments on D-br-A compound **2** in alkane solvents, we conclude that the intramolecular charge separation process is accompanied by a very large contraction. Since the molecule itself can be considered to be rigid, the contraction can only be attributed to electrostriction of the solvent around the highly dipolar D^+-br-A^- species. According to simple electrostatic theory, this effect depends on solvent compressibility, and thus on alkane chain length and temperature, which could be confirmed experimentally. At the same time, the solvent-dependence of the structural volume change strongly complicated quantification of the results, necessitating a new approach to the data evaluation. The most-reliable values resulted from an "isocompressibility" plot (Figure 6), yielding an enthalpy content of $\Delta H_{\rm CT} = (286 \pm 36)$ kJ/mol for the CT state of **2** and a contraction upon charge separation of (-160 ± 30) mL/mol in *n*-heptane at room temperature. Volume changes across the alkane range studied (from *n*-hexane to *n*-dodecane) were estimated as -200 to -110 mL/mol, depending on alkane and temperature. These contractions are an order of magnitude larger than those reported for other D-br-A compounds,[4,16] and can be explained by the much larger dipole moment of the CT state of **2**. Interestingly, this indicates that the reorganization in nonpolar media depends largely on the properties of the D-br-A molecule, which organizes its surroundings by means of electrostatic forces.

Acknowledgment. We thank Sigi Russell for her technical assistance with the LIOAS experiments, Dagmar Lenk for extending our deconvolution program with an improved shift option, and Dr. Anja Remberg for valuable suggestions on mathematical minimization procedures. Furthermore, Dr. Martin Roest and Prof. Jan Verhoeven are thanked for providing useful information on their various triplet yield studies on D-br-A systems. Support from the Australian Research Council (to M.N.P.-R.) is gratefully acknowledged. Finally, we are indebted to Prof. Kurt Schaffner for his constant interest and support.

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