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Temperature-Dependent Electron-Transfer Quenching of Dye Monomer Fluorescence on Octahedral AgBr Grains

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Abstract: At very low coverage, in the range of 0.005, fluorescence decay of dye molecules, 3,3′-diethylthiacarbocyanine iodide, is independent of coverage on the (111) face of monodisperse octahedral AgBr grains in a gelatin emulsion. Fluorescence decay of the adsorbed monomers is monoexponential from room temperature down to 5 K. The decay time increases from 56 ps at room temperature to 550 ps at 100 K, and it remains constant below 100 K. When the decay is fast, ground-state dye molecules are consumed and silver clusters are formed in the AgBr grains. The short decay times above 100 K are attributed to electron transfer from the excited singlet state of adsorbed dye monomers to the empty conduction band of AgBr. The rate constant shows an exponential increase with rising temperature, i.e., Arrhenius behavior. The activation energy is 0.09 eV and the preexponential factor is $3.2 \times 10^{11}\ s^{-1}$. In the nonadiabatic limit we arrive at an electron-transfer integral of 27 cm^{-1}. The excited donor orbital of the dye monomers lies at the lower edge of the conduction band of the octahedral AgBr grains.

Introduction

Electron transfer from the excited singlet state of an adsorbed molecule to the conduction band of semiconductors with a wide band gap is the only heterogeneous electron-transfer reaction that has been measured until now with picosecond time resolution. It has been studied with optical and electrical[2] measuring techniques. Apart from its fundamental importance for testing theories of interfacial electron transfer, this type of reaction plays a decisive role in the photographic process[3] and in a new type of solar cell.[4] The rate constant of this light-induced reaction can give information on the strength of the electronic coupling of adsorbed molecules to the surface of semiconductors. The latter information is also interesting for certain chemical sensors.[5]

Fluorescence of adsorbed molecules can be measured with picosecond resolution even for excitation with extremely weak laser pulses. Electron injection via light-induced interfacial electron transfer can be detected as corresponding photocurrent when the active interface serves as an electrode in a suitable electrochemical or solid-state circuit. This dye-sensitized photocurrent is well-known in the field of stationary photoelectrochemistry at semiconductor electrodes.[6] It is now widely accepted that the same type of reaction, i.e., electron transfer from the excited singlet state of adsorbed dye molecules to the conduction band of AgBr, is the primary step in silver-halide photography.[3] In contrast to the photoelectrochemical cells, there is no regeneration agent added to the photographic system. Oxidized dye molecules are reduced only via a recombination reaction, and they remain in the oxidized state if the injected electrons are consumed in the production of silver clusters in the AgBr grains. Irreversible oxidation of the adsorbed dye molecules can lead to the gradual disappearance of absorption and fluorescence signals when the system is exposed to a high photon flux.

Different authors have observed different fluorescent decay curves for interfaces built from the same chemical components (compare ref 27 given in ref 1). Most likely, there is a great variation in the properties of these interfaces unless they are prepared from identical materials following the same rigorously reproducible procedure. To our knowledge, there is no systematic experimental study of a heterogeneous electron-transfer reaction available until now, which would show the theoretically expected Arrhenius-type temperature dependence and the expected preexponential factor in the range $>10^{12}\ s^{-1}$. The latter range of values should apply when there is direct contact between adsorbate and substrate.[1,7] Such an experiment is particularly valuable when the rate constant is measured over a large range of temperatures and when the activation energy of the reaction is small. Clearly, the interpretation of the opposite case, i.e., of a small rate constant measured over a narrow temperature range, is much more ambiguous since many different effects can make a reaction slow. Fast electron transfer in the picosecond window can be measured most conveniently when either the donor or the acceptor state is prepared by photon absorption. The experiment can be carried out such that the measured fluorescence decay is controlled by the rate constant for electron transfer from the excited electronic state of the adsorbed dye monomers to the surface of the semiconductor. This holds true when the following three requirements are fulfilled. Firstly, the dye coverage has to be extremely low to address the situation where individual adsorbed molecules, e.g., dye monomers, perform the reaction. At higher coverage the interpretation of time-resolved optical or elecrical signals can become very involved and ambiguous due to migration, trapping, quenching, and release of the excitation energy,[8] and to electron injection from trap states formed by aggregates.[9] Secondly, the dye monomers should be adsorbed on sites with an identical rate constant for electron transfer. A distribution of different rate constants can lead to nonexponential decay and make the evaluation of the decay curve ambiguous. The latter situation is rather the rule than the exception for fluorescence decay curves of adsorbed molecules which are mostly multiexponential.[8] Thirdly, in order to eliminate the influence of an activation energy on the speed of electron transfer, the ionization energy in the vibrational ground state of the excited adsorbed dye monomer, acting as donor, must be placed above the semiconductor's lower

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(1) Willig, F.; Eichberger, R.; Sundaresan, N. S.; Parkinson, B. A. *J. Am. Chem. Soc.* **1990,** *112,* 2702.

(2) Bitterling, K.; Willig, F. *J. Electroanal. Chem.* **1986,** *204,* 211.

(3) West, W.; Gilman, P. In *Theory of the Photographic Process,* 4th ed.; James, T. H., Ed.; MacMillan: New York, 1977; p 251.

(4) O'Regan, B.; Grätzel, M. *Nature* **1991,** *353,* 737.

(5) Tieke, B. *Adv. Mater.* **1991,** *3,* 532, and references quoted there.

(6) Gerischer, H.; Willig, F. In *Topics in Current Chemistry;* Boschke, F., Ed.; Springer: Berlin, 1976; Vol. 61, p 31.

(7) Nordlander, P.; Tully, J. C. *Phys. Rev. Lett.* **1988,** *61,* 990.

(8) (a) Kemnitz, K.; Murao, T.; Yamazaki, I.; Nakashima, N.; Yoshihara, K. *Chem. Phys. Lett.* **1983,** *101,* 337. (b) Willig, F.; Blumen, A.; Zumofen, G. *Chem. Phys. Lett.* **1984,** *108,* 222.

(9) (a) Eichberger, R.; Willig, F. *Chem. Phys.* **1990,** *141,* 159. (b) Willig, F.; Eichberger, R.; Bitterling, K.; Durfee, W. S.; Storck, W.; Van der Auweraer, M. *Ber. Bunsenges. Phys. Chem.* **1987,** *91,* 869.

(10) Kietzmann, R.; Willig, F.; Weller, H.; Vogel, R.; Nath, D. N.; Eichberger, R.; Liska, P.; Lehnert, *J. Mol. Cryst. Liquid Cryst.* **1991,** *194,* 169. We have carried out several detailed studies of the concentration dependence as described in this paper, involving small semiconductor particles and also spherical AgBr grains. With all these systems we did not succeed in reaching the ideal monoexponential decay even at very low dye coverages.

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conduction band edge with an energy difference greater than the reorganization energy of the reaction.[1,6] When chosing the experimental system on the basis of reference data, i.e., the standard oxidation potential, the singlet excitation energy of the dye, and the conduction band edge of the semiconductor, the desired energetic relationship can only be approached with some uncertainty, since the energy levels can be shifted at the actual interface with respect to the available reference data.

The photographic industry has achieved a remarkable expertise in preparing with wet-chemistry methods a well-behaved interface that comes close to the above requirements. We report here on the best system we have found which consists of octahedral AgBr grains with about 1-μm diameter. These octahedral microcrystals expose only the (111) plane at their surface[11] to the dye molecules added to their gelatin environment. This offers the possibility of adsorbing dye monomers on identical sites. The unambiguous fingerprint of this desired situation is monoexponential decay of the dye fluorescence, where the time constant remains the same and only the amplitude of the signal changes with dye coverage. In this paper we present such fluorescence decay curves of dye monomers adsorbed on the (111) face of octahedral AgBr grains. Luminescence at very low dye coverage is used as a reference signal. It is subtracted from the luminescence signals measured at slightly higher dye coverages to obtain the desired signal stemming only from the adsorbed dye monomers. The resultant difference curves show monoexponential decay. In the range of very low dye coverages, the time constant of the difference curve remains identical and only its amplitude follows an increase in dye coverage.

At room temperature the fluorescence decay time of the adsorbed dye monomers is short, i.e., 56 ps. It becomes longer with decreasing temperature, reaching 550 ps at 100 K, and below 100 K it remains constant. Fast electron-transfer quenching of the excited dye monomers is expected to take place in this system, judging from the position of the donor level of the excited dye monomers in solution[12] and from the position of the conduction band edge of AgBr.[13] Above 100 K, fluorescence gradually disappears and light-scattering changes with on-going exposure of the sample to light. These effects are known to indicate the formation of silver clusters via capture of electrons by Ag^+ ions in the AgBr grains. Oxidation of the dye molecules must obviously lead to a decrease in the fluorescence signal, and the growth of silver clusters in the emulsion is known to cause an apparent increased light absorption in the visible spectral range.[14] Therefore, we attribute the short fluorescence decay times above 100 K to thermally activated electron-transfer quenching of the excited singlet of the adsorbed dye monomers. The rate constant of electron transfer shows a nice Arrhenius-type temperature dependence with an activation energy of 0.09 eV and a preexponential factor of 3.2×10^{11} s^{-1}. To our knowledge, this is the first set of rate constants for a fast heterogeneous electron-transfer reaction showing monoexponential decay over a wide range of temperatures. The small activation energy shows that the donor level of the excited singlet state of the adsorbed dye monomer lies close to the conduction band edge at the surface of AgBr. The relatively low value for the preexponential factor is attributed to a nonadiabatic reaction mechanism.

Experimental Section

The dye-sensitized emulsions were prepared through adsorption of the dye 3,3′-diethylthiacarbocyanine iodide onto a 1.1-μm monodisperse octahedral AgBr photographic emulsion. Figure 1 shows a micrograph of the octahedral AgBr grains. The surface area of the emulsion was 1.3 m^2/g of Ag. The pH of the emulsion was 6.3 and its pAg 8.5. The gelatin/Ag weight ratio of the emulsion was 0.44/L. In the preparation of the sensitized emulsion, a trifluoroethanol solution of the dye was added to the heated, liquid emulsion at a volume of 0.13 mL of dye solution per gram of emulsion. The concentration of the dye solution was varied to obtain the desired surface concentration. After addition of the dye, the emulsion was held at 40 °C for 1 h. For the fluorescence measurement the emulsion was spread as a 0.2-mm thick layer on a quartz slide (Suprasil). The layer could be used immediately after the gelatin had set, called "wet", or after drying in a dessicator. Drying consisted of a 48-h exposure in a dessicator at 22 °C, at which time there was no further weight change in the sample. Except in the comparison of the fluorescent decay of the "wet" versus "dry" samples, all samples used in these experiments were in the "dry" condition.

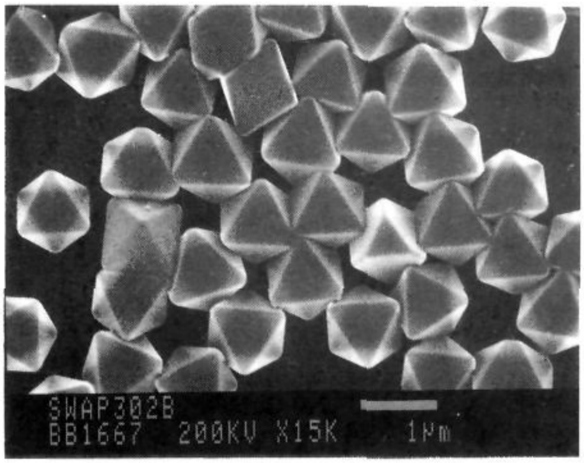

Figure 1. Electron micrograph of the octahedral AgBr grains with a diameter of 1.1 μm.

The light source was a cavity dumped picosecond-dye laser (Spectra-Physics 375, 344S) driven by a mode-locked Ar ion laser (171). The incident laser beam contained 5×10^{10} photons per pulse at 590-nm wavelength; it had a 8-ps pulse width (as measured with Autocorrelator 409) and a 400-kHz repetition rate. To measure the fluorescence decay curves with negligible dye bleaching in the sample, the laser beam was attenuated by a factor of 4×10^4 with neutral gray density filters and focussed on a 0.25-mm^2 spot. Fluorescence emission was measured at 90° to the incident laser beam. Scattered laser light was blocked with cutoff filters (Schott RG 630). The fluorescence decay curve was obtained with time-correlated single-photon counting[15] (SPC). Fluorescence was detected with a Hamamatsu microchannel plate photomultiplier (R 2809-01), a preamplifier (ESN Electronic VT 110 CH4), a constant fraction discriminator (Ortec 943), a time-to-amplitude converter (Ortec 457), and a multichannel analyzer (Norland 5400). The start pulse was generated by a fast avalanche photodiode (Coherent). Data were stored and plotted with an IBM PC. The apparent laser pulse width (fwhm) measured with the SPC apparatus was shorter than 40 ps. The sample was mounted in a He cryostat (Cryo Vac, Konti IT, Spectro 4) with a temperature range from 300 to 1.5 K.

All experimental work was performed in the dark. The total light exposure of the sample during an experimental would result in loss of less than 5% of the adsorbed dye if every photon incident on the sample led to oxidation of a dye molecule. It turned out that the safest procedure was shifting the laser spot to a different position on the surface of the sample, and of the reference (compare Experimental Results section), before recording the next decay curve. Bleaching of the sample sets an upper limit to the total number of phonons the sample can be exposed to without changing the nature of the emulsion via bleaching, i.e., oxidation, of the dye molecules adsorbed on the surface of the AgBr grains.

Experimental Results

Migration of the excitation energy and subsequent trapping and quenching at aggregates become insignificant when the distance between adsorbed dye molecules becomes very large at very low dye coverage. The fluorescence decay curve of isolated adsorbed dye molecules can become monoexponential if the monomers occupy identical surface sites. We shall see below that this ideal experimental situation was reached at very small dye coverages.

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(11) Eggers, J.; Haase, G.; Matejec, R. *Physikalische und chemische Eigenschaften der Silberhalogenide und des Silbers*; Akademische Verlagsgesellschaft: Frankfurt, 1968.

(12) (a) Lenhard, J. *J. Imag. Sci.* **1986**, *30*, 27. (b) The excitation energy is estimated from the crossing point of the absorption and fluorescence spectrum of the dye on AgBr grains. (c) Rehm, D.; Weller, A. *Ber. Bunsenges. Phys. Chem.* **1969**, *73*, 834.

(13) Gilman, P. B., Jr. *Photogr. Sci. Eng.* **1974**, *18*, 475.

(14) Klein, E.; Metz, H. J. *Photographic Sci. Eng.* **1961**, *5*, 5.

(15) O'Connor, D. V.; Phillips, D. *Time-Correlated Single Photon Counting*; Academic Press: New York, 1984; note in particular p 270.

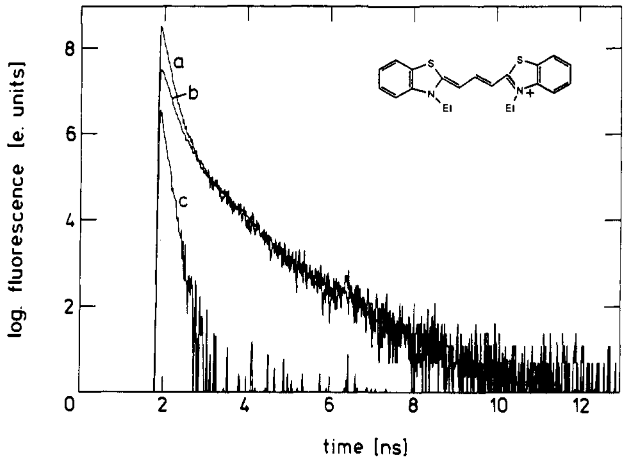

Figure 2. Procedure for obtaining the fluorescence difference curve of an incremental amount of adsorbed dye molecules: (a) decay signal measured with 4 × 10^{-9} mol/g of Ag (formal coverage of 0.002) in the emulsion, (b) reference decay signal measured with 2 × 10^{-9} mol/g of Ag (formal coverage of 0.001), (c) difference curve (a) - (b) due to fluorescence of adsorbed dye molecules. A more precise difference curve was obtained from the second curve-fitting procedure explained in the text.

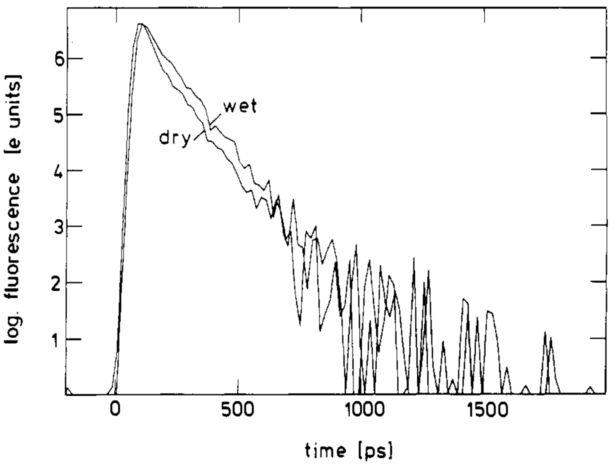

Figure 3. Experimental difference curves (compare Figure 2) with lifetime of 56 ps of an emulsion in its "wet" and "dry" state, i.e., before and after drying in a desiccator. The emulsion contained 4 × 10^{-9} mol of dye/g of Ag (formal coverage of 0.002).

To eliminate luminescence of other origin than from an incremental fraction of adsorbed dye molecules, we measured at a given temperature the luminescence decay of the actual sample and as a reference the luminescence decay signal that was recorded at the extremely low dye concentration of 2 × 10^{-9} mol/g of Ag. Assuming an area of 100 Å^2 for each adsorbed dye molecule, the latter dye concentration is equivalent to a formal surface coverage of 0.001, given the surface area of the emulsion of 1.3 m^2/g of Ag. The initial part of the fluorescence decay curve was fast and grew in amplitude when the dye concentration was increased in small steps to 4 × 10^{-9}, 8 × 10^{-9}, and 16 × 10^{-9} mol of dye/g of Ag, or for the formal dye coverage 0.002, 0.004, and 0.008. The shape of this fast initial part remained identical, independent of dye coverage. Subtracting the reference decay curve of the 2 × 10^{-9} mol/g of Ag sample, we obtained the experimental difference curve for fluorescence decay of the incremental amount of adsorbed dye molecules. Such an experimental difference curve is shown in Figure 2. This way, the superimposed luminescence signals that are contributed by other nondye luminescent centers in the sample are eliminated. The difference curve is meaningful when all the dye molecules are adsorbed on the AgBr grains, and there is no noticeable fluorescence from dye molecules left in the gelatin. In the ideal case the decay of the difference curve is monoexponential when only dye monomers are adsorbed on identical surface sites.

Monoexponential decay of the fluorescence emitted by the incremental dye coverage was established by carrying out the following two different curve-fitting procedures. In the first procedure we subtracted the two experimental curves, for sample and reference, and fitted the remaining data points firstly with a monoexponential and secondly with a biexponential trial function, applying each time the convolution with the response function measured for the laser pulse alone. The actual curve fitting was carried out with the NL2SOL modular program.[16] The biexponential fits did not yield significantly better χ^2 values than the monoexponential fits. Moreover, there was a huge random fluctuation in the amplitudes and time constants for the second exponential in the biexponential fits for the data obtained at different temperatures. Since there is no meaningful physical picture that could explain such huge random fluctuations, we consider these random fluctuations of the second exponential as an indication of some remaining systematic scatter in the data. In many of the fits the amplitude of the second exponential entered with a value 10^{-3} times the amplitude of the first exponential, i.e., with the magnitude of the subtracted reference curve. The following second curve fitting procedure gave better χ^2 values than the first. The complete experimental decay curve of the sample was fitted by adding firstly a monoexponential or secondly a biexponential decay trial function on top of the respective complete experimental decay curve of the reference. Two experimental data sets, each with Poisson distributed errors, contribute to the variance.[15] The added trial function is now the difference curve. Again there was no systematic improvement in the χ^2 values when adding the biexponential as against the monoexponential trial function. The amplitude of the second exponential was in many cases 10^{-3} times the amplitude of the first exponential component. The time constants of the second exponential varied in the fits nonsystematically between 500 ps and some μs. With the second curve-fitting procedure, only 4 out of the 40 decay curves of sample and reference at the different temperatures gave χ^2 values >1.3, and the others gave χ^2 values <1.3 with the monoexponential trial function. On the basis of these fits, we conclude that the monoexponential behavior of the difference curve is established, since the biexponential trial function gave neither a significant improvement in the χ^2 values nor did it show any sensible trend for the amplitudes and time constants of the second exponential component when the temperature was varied. Thus, we attribute the difference curve to the monoexponential fluorescence decay of an incremental number of dye monomers added on the surface of the sample in the range 0.005 of a formal coverage, where we assume that each dye monomer occupies an area of 100 Å^2. A direct measurement of the stationary fluorescence emitted by the incremental dye coverage was not possible in view of the huge additional luminescence emitted by the samples. The stationary fluorescence signal was approximated by integrating the difference curve over time.

(a) Difference Curve of the Wet and Dry Emulsion. Temperature is one of the most important parameters controlling the speed of the electron-transfer reaction. Temperature can be varied in conveniently small steps, which is difficult for other important parameters like the standard free energy change of the reaction. A straightforward interpretation of the temperature dependence is possible if all the other parameters remain constant when the temperature is changed. To achieve this situation we used "dry" samples, prepared as described above, in temperature studies in a cryostat. Comparisons were made with "wet" samples at room temperature. We could not predict what influence this drying procedure would have on the important dynamic parameters of the electron-transfer reaction: the reorganization energy, the electronic tunneling barrier, and the standard free energy difference. The experimental difference curves obtained by subtracting the data for luminescence decay of sample and reference are shown in Figure 3. The emulsion gives very similar expo-

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[16] Dennis, J. E.; Gay, D. M.; Welsch, R. E. ACM *Trans. Math. Software* **1981**, *7*, 348, 369.

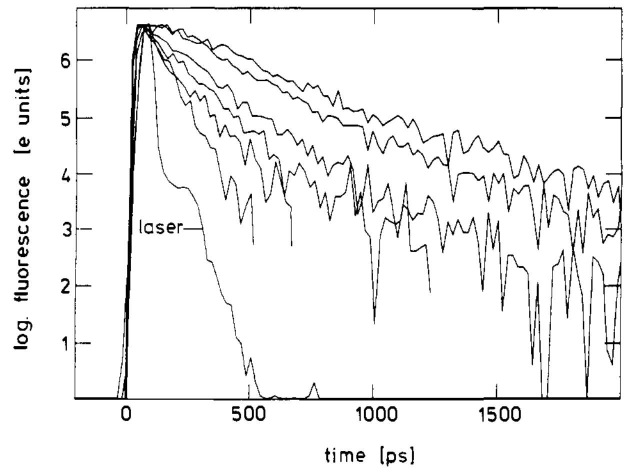

Figure 4. Temperature dependence of the difference curve. The apparent shape of the laser pulse and of difference curves determined as in Figure 2 at various temperatures (from top to bottom): 160, 200, 220, 240, 280, and 300 K. The decay parameters of the difference curves were determined from the second curve-fitting procedure explained in the text.

nential difference curves in its "wet" and "dry" state with a lifetime of 56 ps in both cases. Note that we used the second fitting procedure outlined above for determining the decay parameters of the difference curves.

(b) Temperature Dependence of the Difference Curve. The temperature dependence of the difference curve was determined with two "dry" coatings mounted on the same sample holder in the He cryostat. At each temperature the decay curves were measurements of a reference emulsion containing 2×10^{9} mol/g of Ag, corresponding to a formal dye coverage 0.001 (s.o.), and of a sample with a higher dye concentration. We chose for the latter 16×10^{-9} mol/g of Ag, corresponding to a formal dye coverage of 0.008 (s.o.), i.e., the highest dye concentration where the shape of the difference curve was still that of the samples with lower dye coverages. Some experimental difference curves obtained by subtracting the data for sample and reference at different temperatures are plotted in Figure 4. The curve-fitting procedures described above proved that their decay was monoexponential between 300 K and 5 K. Between 300 K and 100 K, the decay time became longer when the temperature was lowered. At and below 100 K, the difference curve remained identical. It should be noted that the decay curves were measured over a much wider time window than shown in Figure 4. The complete data over the whole measured time window were utilized in the second of the above-described curve-fitting procedures, whereas the curves in Figure 4 were obtained by subtracting the data for sample and reference. The laser pulse measured under identical experimental conditions is also shown in Figure 4. A logarithmic plot of the decay times, as obtained with the second curve-fitting procedure described above, against the reciprocal temperature is given in Figure 5. The decay time increased steeply from 56 ps to 550 ps when the temperature was lowered from 300 K to 100 K, and it remained constant when the temperature was further decreased to 5 K. We have not inserted error bars into Figure 5. It is well known that the small variance determined for the decay time from the above-described curve-fitting procedures in not meaningful.[15] We measured the temperature dependence of only a few samples and reference samples and cannot offer any statistical data on the scatter between different samples. This would be difficult to obtain since preparation with wet chemistry methods cannot avoid slight systematic differences between different samples.

(c) Photobleaching of Adsorbed Dye Molecules. Under the extremely low light level conditions of the experiments described above, we can neglect the irreversible oxidation of adsorbed dye molecules. The magnitude of the stationary fluorescence signal from adsorbed dye molecules follows the change in lifetime of the difference curves for different temperatures shown in Figure 5. The behavior of the sample was very different when the peak power of laser beam was increased by five orders of magnitude. Neutral gray density filters were removed to reach 2-mW pseudostationary power. Under these conditions, regeneration of oxidized dye molecules was incomplete and injected electrons reduced Ag^+ ions to form Ag nuclei on the AgBr, i.e., clusters of "print-out" silver increasing in size.[14,17] There is a concomitant, irreversible conversion of adsorbed dye molecules to their oxidized state. Figure 6 shows a corresponding measurement with high peak power of the incident laser beam, i.e., 2-mW quasi-stationary laser power at a repetition frequency of 400 kHz. Bleaching of the adsorbed dye molecules is monitored as gradual disappearance of dye fluorescence with on-going light exposure. Measurements at different light intensities revealed that the time constant for the fast initial decay in Figure 6 decreases with increasing power of the quasi-stationary laser beam. This is, of course, expected for the bleaching process. The much slower additional decay of the quasi-stationary fluorescence signal seen in Figure 6 is not due to fluorescence of adsorbed dye molecules. It stems from luminescent processes occurring in the bulk of the AgBr crystallites or in the gelatin and can be removed by applying a difference procedure similar to the one described above. Parallel to bleaching of the dye molecules was a reduction in the laser light that was scattered into the detector. This apparent increase in the absorption coefficient for light in the visible range is a well-known effect arising from Mie scattering when silver clusters grow in the emulsion.[14,17]

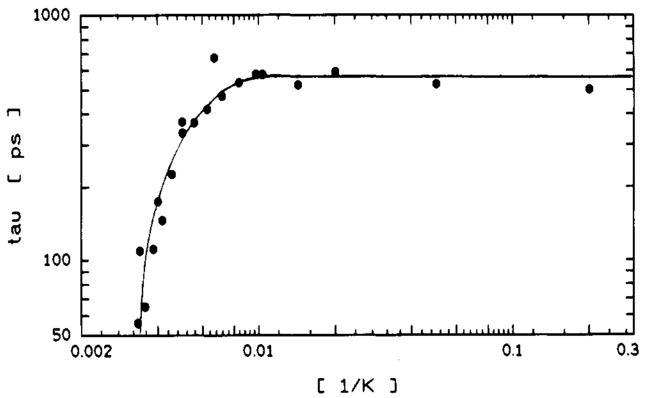

Figure 5. Logarithmic plot of the lifetime τ of the difference curve against reciprocal temperature. The lifetimes were determined with the second curve-fitting procedure explained in the text. The lifetime increases steeply from 300 to 100 K and remains constant from 100 to 5 K. The solid curve is drawn as guide to the eye.

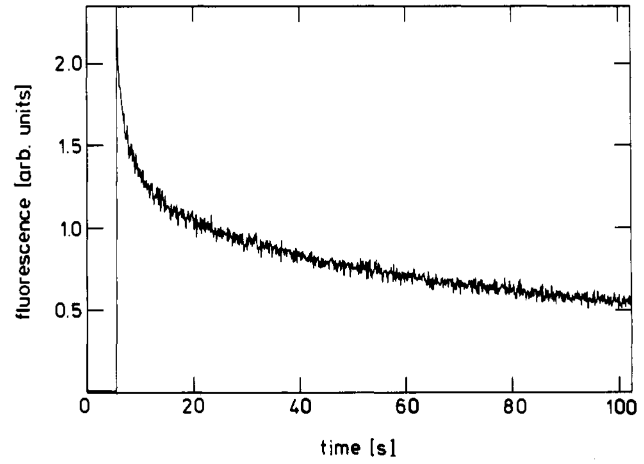

Figure 6. Photobleaching of adsorbed dye molecules. Bleaching of adsorbed dye molecules was monitored as gradual disappearance of the quasi-stationary dye fluorescence with on-going light exposure. The peak power of the laser beam was increased to reach 2-mW pseudo-stationary power. This is more than a factor of 10^5 higher than applied for the measurements illustrated in Figure 2–4.

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(17) Kruse, M. A. In *Theory of the Photographic Process*; James, T. H., Ed.; McMillan: New York, 1977; p 592.

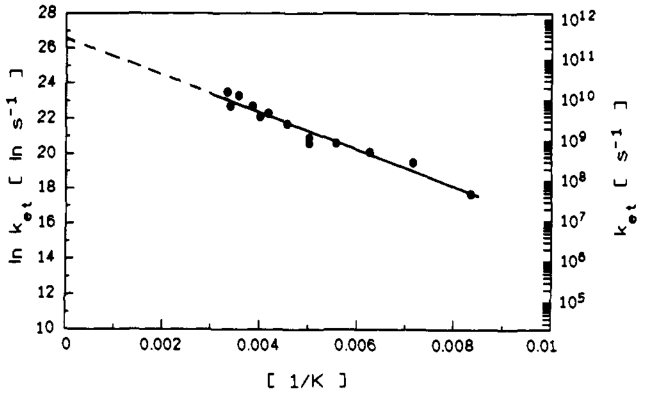

Figure 7. Arrhenius relationship for the rate constant $k(T)$ obtained from the lifetimes $\tau(T)$ of the respective difference curves at different temperatures, applying $1/\tau(T) = 1/\tau_r + k(T)$. A least-squares deviation fit to the Arrhenius plot gives a free activation energy of $\Delta G^* = 0.09$ eV and a preexponential factor $A = 3.2 \times 10^{11}$ s^{-1}.

Discussion

In the Experimental Results section we have presented fluorescence decay curves of dye molecules adsorbed on the surface of the wide band gap semiconductor AgBr. These decay curves have been obtained through time-correlated single photon counting which is a standard, sensitive technique for measuring picosecond-resolved luminescence signals.[15] The significance of our experiments lies, firstly, in the extension of such measurements to the range of extremely low dye coverages; secondly, in the employment of a reference signal that enables us to determine the signal due only to adsorbed dye monomers; thirdly, in the use of octahedral AgBr crystallites that offer identical adsorption sites on the (111) surface; and, fourthly, in the establishment of a correlation between light absorption and bleaching of the adsorbed dye molecules. The combination of these points allows us to interpret monoexponential fluorescence decay curves of adsorbed dye monomers measured over the whole temperature range from 300 K to 5 K and to determine the temperature dependence of the rate constant of electron transfer between 300 K and 150 K.

A straightforward interpretation of the experimental curve in Figure 5 leads to a self-consistent result. The constant decay time τ_r, appearing in Figure 5 at temperatures below 100 K, can be identified with the decay time in the absence of electron-transfer quenching of the adsorbed dye monomers. The time integral over the difference curve indicates that this contribution to the decay is also present at temperatures above 100 K. The decrease in the total lifetime seen in Figure 5 for temperatures above 100 K is attributed to a thermally activated electron-transfer quenching of the exicted dye monomers. Thus, the measured lifetime is interpreted as follows:

$$1/\tau(T) = 1/\tau_r + k(T) \qquad (1)$$

Applying eq 1, we determined the rate constant of electron transfer $k(T)$ from the data in Figure 5. The high-temperature limit of electron-transfer theory predicts an Arrhenius relationship for $k(T)$.[18]

$$\ln k(T) = \ln A - \Delta G^*/k_B T \qquad (2)$$

This is clearly seen to be valid for the present experimental system from the corresponding plot of the experimental data in Figure 7. Applying eq 2, we determine from the experimental data, by a least-squares deviation fit, firstly, the free activation energy of the reaction $\Delta G^* = 0.09$ eV and, secondary, the preexponential factor $A = 3.2 \times 10^{11}$ s^{-1}. We have not inserted error bars into Figure 7. The error bars determined for the fit parameters from curve-fitting procedures are known to be unreasonably small.[15] An error in the value of the time constant τ_r has little influence on the rate constant at high temperatures in Figure 7, but its influence becomes more and more significant when the data points approach 150 K. We consider the proximity of the data points also in this range of lower temperatures to the fitted straight line in Figure 7 as fortuitous. The free activation energy ΔG^* can be expressed as in eq 3,[18]

$$\Delta G^* = (\Delta G_0 + \lambda)^2/4\lambda \qquad (3)$$

since the experimental data in Figure 7 support application of the high-temperature approximation for $k(T)$.

We have also fitted the experimental data with a model taking into account an energy-dependent density of states in the conduction band of the semiconductor. Because of the steep dependence of the rate constant on the energy difference ΔG_0, we arrived at a virtually identical result; i.e., the rate constant corresponds to transitions in a very narrow energy range close to the conduction band edge. In electrochemistry the validity of this simpler approximation has been well known for a long time.[19]

Considering that the dye monomers are adsorbed on the surface of a solid and that the gelatin environment shows solid-like behavior (compare Figure 3), we attribute most of the reorganization energy involving the gelatin side of the interface to λ_i, the so-called inner sphere reorganization of the dye molecule,[20] involving changes in the lengths and angles of the bonds. The same conclusion of a negligible λ_0, i.e., a negligible contribution to the reorganization energy from the medium around the adsorbed dye monomer, is reached from an electrostatic estimate applying Marcus' equation[21] for a spherical molecule at the boundary between two dielectric media. The optical dielectric constant of gelatin[22] is of the order of 2, and we assume that its static dielectric constant is not very different. The static and optical dielectric constants[23] of AgBr, i.e., 12.5 and 4.6, are much larger than the corresponding values for gelatin. Thus, an estimate with Marcus' electrostatic model[20] for λ_0 predicts that there should be a very small value of λ_0 for the dye incorporated into the gelatin environment and about half of that very small value at the interface with AgBr. We assume the following limits for the total reorganization energy: $\lambda = \lambda_0 + \lambda_i$, 0.2 eV $< \lambda <$ 0.6 eV.[24]

Inserting these values for λ into eq 3, we obtain corresponding limits for the standard free energy difference, -135 meV $< \Delta G_0 < 70$ meV. The standard redox energy level of the excited singlet states of the adsorbed dye monomers as donors lies by ΔG_0 away from the energy of the electronic acceptor levels at the (111) surface of the AgBr crystallites that we identify with the lower edge of the conduction band. The standard oxidation potential of the dye in acetonitrile is 0.90 V versus Ag/AgCl,[12a] and the energy of its excited singlet state on AgBr is about 2.1[12b] eV, suggesting a "standard oxidation potential in the excited singlet state"[12c] somewhere around -1.2 eV versus Ag/AgCl, ignoring a possible shift of the oxidation potential between acetonitrile and the adsorption site on the AgBr grain. The conduction band of AgBr is at about 3.37 eV below vacuum, and this is usually correlated with -1.3 to -1.4 V versus Ag/AgCl in the electrochemical scale.[13] These latter values predict that the above standard free energy difference ΔG_0 should be very small, in qualitative agreement with the small value determined for ΔG_0 from the measured temperature dependence of the rate constant. We accept this agreement as an empirical fact, since it is very difficult to make a realistic assessment of the change in the standard redox potential when moving the dye monomers from the solvent acetonitrile to their adsorption sites on the (111) surface of the octahedral AgBr crystallites in the emulsion. Many detailed

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(18) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679; **1984**, *81*, 4494. (b) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (c) Islampour, R.; Lin, S. H. *J. Phys. Chem.* **1991**, *95*, 10261.

(19) Gerischer, H. *Z. Phys. Chem. (Frankfurt/Main)* **1961**, *27*, 49.

(20) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 679. Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

(21) Marcus, R. A. *J. Phys. Chem.* **1990**, *94*, 1050, eq 8 and 16.

(22) Wolfe, R. N.; DePalma, S. B.; Saunders, S. B. *J. Opt. Soc. Am.* **1965**, *55*, 956.

(23) Hamilton, J. F. *Adv. Phys.* **1988**, *37*, 359.

(24) Gaines, G. L., III; O'Neil, M. P.; Svec, W. A.; Niemczyk, M. P.; Wasielewski, M. R. *J. Am. Chem. Soc.* **1991**, *113*, 719. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047.

effects have to be considered, for example, the stabilization of the (111) surface of the AgBr grains by the adsorbed bromide[11] and the proper local charge distribution around the adsorbed dye molecules. Among the above-mentioned plausible values for λ, we favor 0.4 eV, thus the corresponding mismatch of $\Delta G_0 \approx 70$ meV for the energy levels at the interface. With a rate constant of 1.8×10^{10} s^{-1}, electron transfer is much faster at room temperature than the competing decay channels for the excited singlet state of the adsorbed dye monomer. Even though the reaction is not strongly downhill, it is still fast enough at room temperature to guarantee very efficient electron injection as is desired for the photographic process.

In the nonadiabatic limit, the preexponential factor A is expressed as follows:[18,25]

$$A = (2\pi/\hbar)H^2(4\pi\lambda k_B T)^{-1/2} \tag{4}$$

with H = electron-transfer integral. In general, the electron-transfer integral H will include several nearest-neighbor acceptor centers, here Ag^+ sites, in the range of 3 to 10 sites depending on the orientation of the adsorbed dye monomer at the surface. Transfer should depend on the overlap of the dye's donor orbital within the wave functions of the delocalized electronic states in the conduction band. The donor orbital of the excited dye molecule is localized and can thus couple to different k states in the conduction band. However, the steep dependence of eq 2 on the energy difference ΔG_0 and the energetic position of the donor orbital at about the edge of the conduction band favor strongly electron transfer to the k states close to the band edge. The electron-transfer integral is generally assumed to decreased exponentially with a typical 1/e distance on the order of 1 Å through space or through a saturated C–C bond. The precise geometry of the adsorption site and the distribution of charges is not known for the present system. For the above range of λ values, eq 4 with $A = 3.2 \times 10^{11}$ s^{-1} gives the electron-transfer integral in the limits 23 cm^{-1} < H < 30 cm^{-1}. These values suggest that the reaction is of the nonadiabatic type. For small molecules adsorbed on metal electrodes, the electron-transfer integral is expected to be at least 100 times larger[7] than the above range of values for H. The following two different effects can lead to a much smaller preexponential factor in the present system than is expected from the electron-transfer integral for direct electronic overlap.

The first possibility involves the participation of intramolecular modes in the reaction. Efrima and Bixon[26] have shown that intramolecular vibrations with $h\omega > k_B T$ can enter into the rate constant as the product of the electron-transfer integral with corresponding Franck-Condon factors. Since in the present system $\Delta G_0 \approx 0$ and $\Delta G^* = 90$ meV, only the Franck-Condon factors of the vibrational ground state of reactant and product $|\langle 0_r|0_p\rangle|^2$, and possibly of the next higher vibrational state of this quantum oscillator, should play a significant role. In such a case the preexponential factor determined from the experiment would refer to the product of the electron-transfer integral with such Franck-Condon factors, corresponding to an effective "phonon dressed" electronic coupling.[25] The above value for H would represent only a lower limit to the value of the electron-transfer integral.

The second argument involves the preparation of the system with wet-chemistry methods. The (111) surface of octahedral AgBr crystallites is stabilized by adsorption of bromide.[11] Already such an adsorption layer of bromide can form a tunneling barrier and limit the magnitude of H. The thickness of such an atomic layer is not sufficient for causing a drastic reduction in the magnitude of the electron-transfer integral. However, a molecular spacer could be unintentionally inserted between the adsorbed dye monomers and the surface of the octahedral AgBr grains. A good idea of the influence of a molecular spacer on the magnitude of the electron-transfer integral can be obtained from experiments where an excited donor molecule is separated by a rigid aliphatic molecular bridge from the acceptor molecule.[27] For example, we have found with picosecond-resolved fluorescence that electron transfer occurs within a few picoseconds through the five C–C bonds of a cyclohexyl bridge. The electron-transfer integral is about 10 cm^{-1} for this bridge molecule linking the excited singlet state of a porphyrin as donor with the ground state of benzoquinone as acceptor.[27d] Model calculations[28] and experimental results[27] suggest that the electron-transfer rate constant increases by about a factor of 3 when the bridge molecule is shortened by one C–C bond. Therefore, we can safely assume that the electron-transfer integral must be greater than 100 cm^{-1} for direct contact between the dye molecule and the surface of AgBr, i.e., in the absence of any unknown molecular layer or spacer. Model calculations for the H atom directly adsorbed on a jellium-type surface predict that electronic interaction energies can vary over a wide range between 0.1 and several eV,[7] depending on the separation and orientation of the donor orbitals at the surface.

Establishment of a nonadiabatic mechanism of electron transfer has the following implications. After absorption of a photon, the adsorbed dye molecule finds itself in a higher excited vibrational level of its first excited singlet state. Next, there is a redistribution of the vibrational energy over the vibrational modes in the excited molecule prior to electron transfer. Afterward, equilibration of the "local temperature" of the excited dye with that of the environment occurs, again prior to electron transfer, since the latter controls the relatively slow 56-ps time constant at room temperature. Apart from the important change in the standard free energy of the reaction, electron transfer from the excited electronic state of the adsorbed dye molecules occurs in this system by the same mechanism that would apply to molecules in their electronic ground state.

Summary

Dye monomers have been found to adsorb on identical sites of the (111) surface of octahedral AgBr crystallites prepared with wet-chemistry methods. A monoexponential fluorescence decay of the adsorbed monomers over several orders of magnitude is recovered when superimposed luminescence of other origin is removed from the measured signal. This is achieved by subtracting the luminescence signal of a reference sample with vanishing dye coverage from the decay curve measured at slightly higher coverage. Rate constants of electron transfer are derived from the time constants of the monoexponential decay curves by subtracting the rate constant for decay in the absence of electron transfer. The temperature dependence of the rate constant shows an Arrhenius behavior between 300 K and 100 K. This is in agreement with the high-temperature approximation predicted by electron-transfer theory. The preexponential factor $A = 3.2 \times 10^{11}$ s^{-1} suggests a nonadiabatic reaction mechanism in the present system. This preexponential factor appears too small for direct electronic interaction between the dye monomer and the conduction band electrons of AgBr. Wet-chemistry preparation could lead to an unintentional insertion of a molecular spacer layer, or, alternatively, a Franck-Condon factor of an intramolecular quantum mode is involved in the electron transfer, leading to the smaller effective "phonon dressed" electronic coupling of the Efrima–Bixon model.[24,25] The small activation energy of 90 meV implies that the donor orbital of the excited dye monomer lies at the edge of the conduction band of the octahedral AgBr grains. This is in suprisingly good agreement with an estimate based on electro-

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(25) Jortner, J.; Bixon, M. *J. Chem. Phys.* **1988**, *88*, 167.

(26) Efrima, S.; Bixon, M. *Chem. Phys.* **1976**, *13*, 447.

(27) (a) Closs, G. L.; Piotrowiak, P.; MacInnis, J. M.; Fleming, G. R. *J. Am. Chem. Soc.* **1988**, *110*, 2652. (b) Oevering, H.; Paddon-Row, M. N.; Heppener, M.; Oliver, A. M.; Cotsaris, E., Verhoeven, J. W.; Hush, N. S. *J. Am. Chem. Soc.* **1987**, *109*, 3258. (c) Leland, B. A.; Joran, A. D.; Felker, P. M.; Hopfield, J. J.; Zewail, A. H.; Dervan, P. B. *J. Phys. Chem.* **1985**, *89*, 5571. (d) von Gersdorf, J.; Huber, M.; Schubert, H.; Niethammer, D.; Kirste, B.; Plato, M.; Möbius, K.; Kurreck, H.; Eichberger, R.; Kietzmann, R.; Willig, F. *Angew. Chem.* **1990**, *102*, 690.

(28) Beratan, D. N.; Hopfield, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 1584. Bertrand, P. *Chem. Phys. Lett.* **1987**, *140*, 57. Plato, M.; Möbius, K.; Michel-Beyerle, M. E.; Bixon, M.; Jortner, J. *J. Am. Chem. Soc.* **1988**, *110*, 7279. Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1989**, *134*, 323. Hu, Y.; Mukamel, S. *J. Chem. Phys.* **1989**, *91*, 6973. Naleway, C. A.; Curtiss, L. A.; Miller, J. R. *J. Phys. Chem.* **1991**, *95*, 8434.

chemical reference data where no correction has been made for the energy shift between the dye monomer in acetonitrile and on the surface of AgBr.

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Striking Similarities between Elementary Silicon and Aluminum Compounds: Monobridged, Dibridged, Trans-Bent, and Vinylidene Isomers of Al_2H_2

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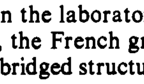
Abstract: Ab initio quantum mechanical methods have been used to study the singlet potential energy surface of Al_2H_2. Optimum geometries and harmonic vibrational frequencies were obtained for four geometrical isomers using the self-consistent-field (SCF), configuration interaction (CI), and coupled cluster (CC) methods. Both correlation methods including single and double excitations (CISD, CCSD) were employed, and all wave functions were determined with both DZP and TZ2P basis sets. Final energy predictions are obtained using large atomic natural orbital basis sets, and including the effects of triple excitations perturbatively using CCSD(T) methods. We found the planar dibridged structure to be the global minimum, as predicted earlier by Baird. However, our analysis also predicts the existence of a remarkable monobridged minimum, which has recently been observed experimentally for Si_2H_2. Two additional low-lying minima are found, corresponding to trans-bent and vinylidene-like structures. The dibridged, monobridged, and trans-bent structures can be understood as resulting from the three possible ways of coordinating the two electron-rich sites of diatomic AlH to the electron-deficient aluminum centers. The energy of these structures with respect to dissociation to two AlH monomers is quite low and is related to the large difference between the first and second Al–H bond dissociation energies of the parent AlH_3 compound.

Introduction

The development of techniques for the synthesis of naked aluminum clusters has increased the possibility of experimental investigations of aluminum hydrides.[1] Such compounds might serve as hydrogen storage devices or may be exploited as low-mass high-energy fuels. Previous theoretical studies[2] of Al_xH_y systems have revealed some of the peculiar characteristics of Al–H bonding, in particular, the role of hydrogen providing bridging bonds between aluminum atoms. Similar structures have been studied in boron,[3–6] aluminum–boron,[7] silicon,[8,9] germanium,[9,10] and gallium[11] hydrides.

The principal motivation for this research is a remarkable recent experimental discovery in the laboratory of Destombes.[12] Via microwave spectroscopy, the French group was able to observe the unconventional monobridged structure (**1**) of Si_2H_2 predicted 2 years earlier in theoretical studies.[8] In those studies, Colegrove[8] predicted **1** to be a genuine minimum on the Si_2H_2 potential energy hypersurface using a triple zeta plus double polarization (TZ2P) basis set in conjunction with the single and double excitation configuration interaction (CISD) method. At the highest level of theory (TZ2P + diffuse + f CISD + Davidson's correction), the unexpected monobridged structure **1** is second only in energy to the nonplanar dibridged ground state[8,13] of Si_2H_2. This result has been confirmed in more exhaustive theoretical studies of Si_2H_2.[14]



(1)

In molecules for which classically bonded alternatives exist (thus, excluding hydrogen bonds, for example), unsymmetrical monobridged structures are rare, and Si_2H_2 is the only one that has been experimentally observed to our knowledge. Such monobridged structures have, however, been found to be low-lying stable minima in theoretical studies of B_2H_4,[3] and Al_2H_4,[2b] and Ga_2H_4,[11] as well as in the heavier group 14 compounds Sn_2H_4 and Pb_2H_4.[9b] Therefore, one goal of the present research was to determine whether the Al_2H_2 system, with two fewer electrons than Si_2H_2, also possesses a low-lying unsymmetrical monobridged molecular structure. A previous study of Al_2H_2 by Baird[2a] optimized only planar trans-bent and doubly bridged singlet states, using the 3-21G* basis set at the SCF level of theory; whether the structures were minima or not was never explicitly stated. We now know that such low-level theoretical studies are incapable

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(1) See, for example: Hamrick, Y. M.; Van Zee, R. J.; Weltner, W. *J. Chem. Phys.* **1992**, *96*, 1767.

(2) (a) Baird, N. C. *Can. J. Chem.* **1985**, *63*, 71. (b) Lammertsma, K.; Guner, O. F.; Drewes, R. M.; Reed, A. E.; Schleyer, P. v. R. *Inorg. Chem.* **1989**, *28*, 313. (c) McKee, M. L. *J. Phys. Chem.* **1991**, *95*, 6519.

(3) Mohr, R. A.; Lipscomb, W. N. *Inorg. Chem.* **1986**, *25*, 1053.

(4) Jouany, C.; Barthelat, J. C.; Daudey, J. P. *Chem. Phys. Lett.* **1987**, *136*, 52.

(5) (a) Sana, M.; Leroy, G.; Henriet, Ch. *J. Mol. Struct.* (*THEOCHEM*) **1989**, *187*, 233. (b) Sana, M.; Leroy, G.; Henriet, Ch. *J. Chim. Phys.* **1990**, *87*, 1.

(6) (a) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *90*, 4314. (b) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 4809. (c) Curtiss, L. A.; Pople, J. A. *J. Chem. Phys.* **1989**, *91*, 5118.

(7) Mains, G. J.; Bock, C. W.; Trachtman, M.; Finley, J.; McNamara, K.; Fisher, M.; Wociki, L. *J. Phys. Chem.* **1990**, *94*, 6996.

(8) Colegrove, B. T.; Schaefer, H. F. *J. Phys. Chem.* **1990**, *94*, 5593.

(9) (a) Trinquier, G. *J. Am. Chem. Soc.* **1990**, *112*, 2130. (b) Trinquier, G. *J. Am. Chem. Soc.* **1991**, *113*, 144.

(10) Grev, R. S.; DeLeeuw, B. J.; Schaefer, H. F. *Chem. Phys. Lett.* **1990**, *165*, 257.

(11) Lammertsma, K.; Leszczynski, J. *J. Phys. Chem.* **1990**, *94*, 5543.

(12) Cordonnier, M.; Bogey, M.; Demuynck, C.; Destombes, J.-L. *J. Chem. Phys.* **1992**, *97*, 7984.

(13) Bogey, M.; Bolvin, H.; Demuynck, C.; Destombes, J. L. *Phys. Rev. Lett.* **1991**, *66*, 413.

(14) Grev, R. S.; Schaefer, H. F. *J. Chem. Phys.* **1992**, *97*, 7990.

0002-7863/93/1515-1936$04.00/0