

19 June 1998

Chemical Physics Letters 289 (1998) 516-520

CHEMICAL PHYSICS LETTERS

# NO product yield excitation spectrum of the $S_0 \rightarrow S_2$ transition of nitrosobenzene in a supersonic jet

Angela Keßler, Uwe Kensy, Bernhard Dick

Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93053 Regensburg, Federal Republic of Germany

Received 17 March 1998; in final form 14 April 1998

#### Abstract

The absorption spectrum of the  $S_0 \rightarrow S_2$  transition of ultracold nitrosobenzene in a supersonic jet was measured indirectly by monitoring the product yield of the NO fragment. The vibrational structure and relative line intensities are in good agreement with the corresponding spectrum in an argon matrix. It is concluded that the yield of photofragmentation is constant for all vibronic  $S_2$ -states up to an excess energy of 3500 cm<sup>-1</sup>. The electronic origin line has a Lorentzian lineshape with a homogeneous width of (90  $\pm$  5) cm<sup>-1</sup>. This corresponds to a lifetime of  $\tau(S_2) = 60 \pm 3$  fs. © 1998 Elsevier Science B.V. All rights reserved.

#### 1. Introduction

Nitrosobenzene has several rather unusual photophysical and photochemical properties. One of these is the large energy gap between the first excited singlet state  $S_1$  and the second excited singlet state  $S_2$ . The  $S_0 \rightarrow S_1$  transition is very weak and occurs in the deep red spectral region. The origin was observed at 11504  $\text{cm}^{-1}$  in the gas phase [1] and at 11442  $\text{cm}^{-1}$  in an argon matrix [2]. The origin of the  $S_0 \rightarrow S_2$  transition has so far only been localized in an argon matrix at 30260  $\text{cm}^{-1}$  [2]. The energy gap between these states  $\Delta E_{12}$  is larger than 18800  $cm^{-1}$ . For the molecule azulene, the origin of the S<sub>1</sub>-state was found in the supersonic jet at 14285  $\text{cm}^{-1}$  [3,4] and that of the S<sub>2</sub>-state at 28757  $\text{cm}^{-1}$ [5]. In this case the energy gap  $\Delta E_{12} = 14473 \text{ cm}^{-1}$ is large enough that fluorescence from the S2-state can be observed. However, in spite of the larger energy gap in nitrosobenzene, no fluorescence from the S<sub>2</sub> state could be identified in this compound [6–8]. An upper limit of  $\Phi_F \le 10^{-5}$  has been estimated for the fluorescence quantum yield in heptane solution by using the spontaneous Raman scattering of the solvent as an internal standard [7]. In the gas phase no signal above the noise level could be detected, leading to  $\Phi_F \le 5 \times 10^{-7}$  [7]. When this was combined with the rate constant for the radiative decay estimated from the integrated absorption spectrum  $(k_r(S_2) \approx 10^8 \text{ s}^{-1})$ , a lifetime of  $\tau(S_2) \approx 10 \text{ fs}$  was estimated [7].

Nitrosobenzene efficiently fragments into an NO radical and a phenyl radical following excitation to the  $S_2$  state. This reaction occurs even at temperatures as low as 10 K in an argon matrix. The phenyl radical in the argon matrix has been identified by IR [9,10] and UV [11] absorption spectroscopy.

The observation of a well resolved  $S_0 \rightarrow S_2$ origin band in the argon matrix in combination with the photochemical activity opened the possibility of a measurement of the homogeneous linewidth with spectral hole-burning. This should yield a much more precise value of the lifetime of the excited state. Unfortunately, it turned out that bleaching of the absorption in the origin band was reversible within a few minutes [2]. This was attributed either to a recombination reaction within the matrix cage, or to a barrier for the photoreaction on the  $S_2$  potential energy surface. In this case the temporal bleaching of the absorption could be explained by the assumption that the excited molecules relax to a metastable matrix site. At higher excitation energies the photoreaction was irreversible, but no spectrally homogeneous subensemble could be selected in this case.

A closer examination of the origin band in the matrix spectrum revealed two shoulders. The red edge could be fitted by a Lorentzian lineshape. In fact, the whole band could be fitted by a superposition of three Lorentzian lines with the same width of  $67 \text{ cm}^{-1}$ . The substructure was attributed to the existence of three matrix sites, although a lowfrequency vibration with a wavenumber of  $\approx 40$ cm<sup>-1</sup> could not be ruled out as an alternative explanation. If residual inhomogeneous broadening and pure dephasing can be neglected, this linewidth corresponds to a lifetime of  $\tau(S_2) \approx 80$  fs. This value is certainly a lower limit to the lifetime in the argon matrix. Apparently there is a discrepancy between this lifetime and the estimate of  $\tau(S_2) \approx 10$  fs obtained from the integrated absorption spectrum and the upper limit of the fluorescence quantum yield in the gas phase. Several reasons could account for this. The lifetime might strongly depend on the vibrational level of the S2-state. The lineshape analysis gives a value only for the electronic origin, whereas the other method yields a value which is averaged over the whole absorption band. The matrix measurement was performed at 15 K whereas the measurements in Ref. [7] were carried out at room temperature. A strong increase in the decay rate with increasing temperature could be due to the existence of a thermally activated decay channel. Alternatively, the lifetime could strongly depend on the environment. The fluorescence quantum yield estimated for the heptane solution is compatible with a lifetime of  $\approx 100$  fs. One could imagine that the rigid matrix cage exerts additional forces upon the molecule which inhibit photodissociation in the vibrational ground state of  $S_2$ . Finally, the fluorescence quantum yield could have been underestimated, or the radiative lifetime overestimated, in applying the Strickler-Berg relation.

Hence it seemed interesting to measure the absorption spectrum of the isolated molecule in the gas phase near the electronic origin of the  $S_0 \rightarrow S_2$  transition. Under these conditions – preferably in a supersonic jet – broadening due to matrix sites and crystal defects are completely absent. This experiment should also answer the question whether nitrosobenzene has a low-frequency mode with a wavenumber of ca. 40 cm<sup>-1</sup> in the S<sub>2</sub>-state or not.

Due to the complete lack of detectable fluorescence from nitrosobenzene in the S2-state a fluorescence excitation spectrum could not be measured. We therefore decided to measure the product yield spectrum of NO as a function of the wavenumber of excitation. The principle of the experiment is apparent from Fig. 1. Cold nitrosobenzene is produced in a supersonic expansion and excited to the S<sub>2</sub>-state by a tunable photolysis laser with wavenumber  $\nu_D$ . The excited nitrosobenzene will dissociate with the quantum yield of dissociation  $\Phi_D$ , forming a phenyl radical and an NO radical. The latter is excited by the probe laser tuned to a characteristic transition of NO at wavenumber  $\nu_{p}$ . The fluorescence following this excitation is monitored and normalized to the pulse energies of the two laser pulses. As long as the excitation steps are not saturated, the resulting spectrum will be the product of the absorption spectrum and the quantum yield of photodissociation of nitrosobenzene into this particular product state of NO.



Fig. 1. Schematic representation of the experiment.  $\nu_D$ : frequency of the tunable photolysis laser.  $\nu_P$ : frequency of the fixed probe laser.

This quantum yield might depend on the excess energy. A barrier to photodissociation would become apparent by a strong increase in this quantum yield above a certain threshold. In this case it might be possible to observe the fluorescence from nitrosobenzene excited below the threshold.

# 2. Experimental

The jet apparatus consists of a single vacuum chamber of 271 mm diameter and 515 mm length which is pumped by the combination of an oil diffusion pump (Levbold DI 3000), a roots pump (Leybold, RUVAC WA 251) and a rotary pump (Leybold Trivac D 65B). Nitrosobenzene was purchased from Aldrich and was used, with the same results, either directly or purified by sublimation. The sample was heated to  $50^{\circ}$ C, seeded into 1.5-2bar of He and expanded through a pulsed valve (General valve No. 9). The photolysis laser and the probe laser are frequency-doubled dye lasers (Lambda Physics LPD 3002 and FL 3002) both pumped by the same XeCl\*-excimer laser (Lambda Physics Lextra 200). The laser beams were aligned to overlap in a counterpropagating geometry. Stray light was eliminated by home-built light skimmers [12]. Fluorescence from NO was collected with a lens (f = 25 mm) and a spherical mirror (R = 60mm) and detected with a photomultiplier (Thorn Emi 9789QA). The laser pulse energies were measured with photodiodes. All signals were integrated with boxcar averagers (Stanford Research Systems SR250), digitized (SR245) and processed by a PC, which also controlled the trigger of the laser and the valve as well as the dye laser scan.

#### 3. Results and discussion

The photodissociation yield was monitored on the  $Q_{12.5}^{11}$  line of the  $A^2\Sigma^+(v'=0) \leftarrow X^2\Pi_{1/2}(v''=0)$  transition of NO. The product-yield excitation spectrum of nitrosobenzene obtained in this way in the spectral region between 30400 and 34400 cm<sup>-1</sup> is shown in Fig. 2 as curve A. It is overlayed, after proper scaling of the vertical axis, with the absorption spectrum of the S<sub>0</sub>  $\rightarrow$  S<sub>2</sub> transition of nitrosobenzene in an argon matrix (J.M. Engert, un-



Fig. 2. (A) NO photoproduct-yield spectrum of nitrosobenzene in the region of the  $S_0 \rightarrow S_2$  transition. (B) Superimposed absorption spectrum of nitrosobenzene in an argon matrix, shifted by 988 cm<sup>-1</sup> to lower wavenumbers (see axis on top). (C) the same matrix spectrum shifted by 0.2 units of intensity for clarity. The jet spectrum was normalized for optimum overlap with the matrix spectrum.

published results). The matrix spectrum was shifted by 988 cm<sup>-1</sup> to higher wavenumbers in order to obtain the best coincidence of the electronic origin bands. The lower abscissa refers to the matrix spectrum, the upper abscissa to the jet spectrum. Apparently both spectra match perfectly. All details of the vibrational structure seen in the matrix spectrum appear also in the jet spectrum. In order to emphasize the similarity of the spectra, which might be obscured by the perfect overlap, the matrix spectrum is displayed a second time shifted by 0.2 units of intensity (curve C).

As long as the two lasers do not saturate the transitions to which they are tuned, the productyield spectrum should be proportional to  $\sigma(\nu_D)\Phi(\nu_D)P_j(NO)$ , where  $\sigma(\nu_D)$  is the absorption cross section of nitrosobenzene,  $\Phi(\nu_D)$  the quantum yield of photodissociation and  $P_j(NO)$  the fraction of NO molecules produced in the particular state monitored by the probe laser. Since, apart from a shift of the spectrum, the absorption spectrum in argon matrix and the photofragment yield spectrum in the jet are proportional to each other, the factor  $\Phi(\nu_D)P_j(NO)$  must be constant over the energy range investigated. We have scanned the excitation spectrum of NO for several fixed values of  $\nu_D$  in the range between 31250 and 34500 cm<sup>-1</sup>. We found that the population of the rotational states of NO was similar in all cases. Hence we conclude that the quantum yield of photodissociation  $\Phi(\nu_D)$  is constant over the whole energy range investigated.

Under the same expansion conditions we found sharp spectra with narrow lines for molecules with long-lived excited states like NO or tetracene. For NO the relative intensities of the few lines observed. correspond to a rotational temperature of 1 K. In the case of tetracene, the width of the rotational envelope was ca.  $1.6 \text{ cm}^{-1}$  and the best fit was obtained for a simulation with a rotational temperature of 8 K. No vibrational hot bands could be found. Hence we believe that the spectrum in Fig. 2 is the spectrum of cold nitrosobenzene. However, all lines and in particular the  $0_0^0$ -line are much broader than the expected rotational envelope. If this linewidth is determined by a short lifetime of the excited state, the shape of the line should be a Lorentzian. A fit of a Lorentzian to the  $0_0^0$ -line, shown in Fig. 3, is indeed in good agreement with the data. The agreement is far better than with a Gaussian lineshape as a trial function. Since the line is apparently homogeneous and since in the absence of collisions and at low temperature the only mechanism for linebroadening is the decay of the excited state, we interpret the width of the Lorentzian (FWHM) of  $\Delta \nu_0 = 90.2 \pm$ 4.6 cm<sup>-1</sup> as the manifestation of an excited state lifetime of  $\tau(S_2) = 60 \pm 3$  fs. The error estimate



Fig. 3. Expanded view of the product-yield spectrum of Fig. 2 in the region of the electronic origin line. The heavy line is a fit of a Lorentzian lineshape with a width (FWHM) of  $\Delta \nu_0 = (90.2 \pm 4.6)$  cm<sup>-1</sup> centered at  $\nu_0 = (31247.9 \pm 0.6)$  cm<sup>-1</sup>.

corresponds to the 95 % probability range, i.e. two standard deviations if a Gaussian distribution of the parameter values is assumed [13]. If further sources of broadening existed, the contribution of the lifetime to the linewidth could only be smaller than 90 cm<sup>-1</sup> and hence a lifetime of  $\tau(S_2) = 60$  fs is a lower limit.

If the lifetime were as small as 10 fs, we would have seen a line width of at least 530  $\text{cm}^{-1}$ . This is inconsistent with the presence of the resolved vibrational finestructure in the absorption spectrum. Apparently the estimate of the lifetime with the help of the Strickler-Berg relation given in Ref. [7] is too small. One source of error could be that the sensitivity of the apparatus was overestimated and hence the value for the quantum yield of fluorescence in the gas phase  $\Phi_F < 5 \times 10^{-7}$  was underestimated. A radiative lifetime of 10 ns and a real lifetime of 60 fs should lead to a quantum vield of fluorescence of  $\Phi_F = 6 \times 10^{-6}$  which is certainly difficult to detect. However, integration of the absorption spectrum can vield a value for the radiative lifetime which is too small if the intensity of the band is mainly borrowed through vibronic coupling from another state. It has been argued that the Strickler-Berg relation can not be applied in such cases [14]. According to our semiempirical CNDO/S calculations the S2-state of nitrosobenzene originates from a doubly excited nn  $\rightarrow \pi^* \pi^*$  configuration [2]. The intrinsic oscillator strength is hence small.

The difference between the lifetimes obtained from the linewidth in the jet (60 fs) and in the matrix (80 fs) is significantly larger than the error estimated from the fitting procedure for each value. The fit yields slightly different results when a linear background is added to the fitting function, but this is not enough to explain the difference. We are, hence, lead to the conclusion that the matrix lengthens slightly the lifetime of the  $S_2$ -state. If the origin line in the jet spectrum were the superposition of three Lorentzian lines, as is the case in the argon matrix, fits of the red edge of the line and of the whole line would yields quite different values for the linewidth. This is, however, not the case. Hence we conclude that the substructure seen in the argon matrix is due to three matrix sites and not the manifestation of a low-frequency mode.

## 4. Conclusions

These observations allow us to draw the following conclusions:

- 1. The electronic origin of the  $S_0 \rightarrow S_2$  transition of isolated nitrosobenzene in the gas phase occurs at 31248 cm<sup>-1</sup>. In an argon matrix, the only other medium in which a vibrational structure of this transition could be resolved so far, the origin is observed at 30260 cm<sup>-1</sup>.
- 2. Since the relative intensities of the vibronic lines in the photodissociation product-yield spectrum of this work perfectly agree with those from the absorption spectrum in an argon matrix, the quantum yield of photodissociation must be constant, at least over the energy range from the electronic origin of the  $S_0 \rightarrow S_2$  transition up to an excess energy of ca. 3500 cm<sup>-1</sup>.
- 3. The statement above is in particular true for the electronic origin line. There is no evidence for a barrier to photodissociation on the potential energy surface of the  $S_2$ -state. The fact that the photobleaching after excitation into the electronic origin band of nitrosobenzene in an argon matrix appears to be reversible must then be due to efficient recombination in the matrix cage.
- 4. The analysis of the lineshape of the electronic origin line yields a homogeneous linewidth of 90 cm<sup>-1</sup> corresponding to a lower limit of the excited state lifetime of  $\tau(S_2) = 60$  fs.
- 5. The substructure of the three lines with similar intensities and a spacing of ca. 40 cm<sup>-1</sup> seen in the argon matrix is not due to a low-frequency mode of nitrosobenzene in the S<sub>2</sub>-state but most likely results from three matrix sites.

From the data presented here it can not be concluded that the photodissociation takes place on the potential energy surface of the  $S_2$ -state. Fast internal conversion to the electronic ground state followed by dissociation on the  $S_0$  potential surface could be an alternative mechanism. In order to clarify this question we have measured the product state distribution of NO for several photolysis energies. The results will be presented in a forthcoming paper.

## Acknowledgements

This work has been supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

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