Subpicosecond relaxation of localized electrons in liquid ammonia

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We report the results of an experimental study of the optical bleaching of the absorption spectrum of the solvated electron in dilute Na–NH_3 and Na–ND_3(2×10^{-4} M) solutions by a single 1.06 μ psec pulse (pulse duration 6 psec, pulse energy 30 mJ). The absorption spectrum of the solvated electron was monitored in the spectral range 1100–850 nm with the time resolution 20–3.3 psec. The line broadening of the solvated electron optical band originates from homogeneous broadening effects. The relaxation time of the excited state of the solvated electron was determined to be $\tau \cong 2\times 10^{-13}$ sec. This ultrashort relaxation time favors relaxation between bound states of the solvated electron center.

I. INTRODUCTION

The wealth of information available on metal–ammonia solutions[1–4] has resulted in a fairly complete understanding of the physical properties of this system. In particular, most dilute solutions (10^{-4}–10^{-3} *M*) exhibit the features of electrolytes containing localized solvated electrons and solvated cations. The currently accepted model[5–10] for the localized solvated electron in polar solvents incorporates both short range attractive and repulsive interactions together with long range polaron-type attractive interactions. This structural model[7–9] resulted in a variety of theoretical predictions for structural and energetic data for the solvated electron, such as ground state configurational stability, the coordination number, volume expansion, heat of solution, photoelectric threshold and photoionization energy dependence. Regarding optical data, the model properly accounts for the position of the maximum of broad absorption band and its temperature and pressure dependence, which is assigned to the bound–bound $1s \rightarrow 2p$ transition of the solvated electron. Some unresolved questions still pertain to the nature of the extremely broad absorption bands which are theoretically underestimated by a numerical factor of 2 both in water and in ammonia.[9] Furthermore, the experimental line shape is definitely skewed towards the high energy side, in contrast to the theoretical curve which is practically symmetrical. This asymmetry may originate for the contribution of higher bound excited states and even bound-continuum transitions.[5,9] This old interpretation is not entirely satisfactory as theoretical estimates indicate that these highly excited states will carry low oscillator strength. It is also possible that the appreciable line broadening originates from inhomogeneous broadening effects, i.e., a large variety of coordination numbers resulting in a continuous distribution of excitation energies due to different trapping centers. There has been recently one proposal[11] for the observed line shape which nets two drastic assumptions: the bound electron is treated as a particle in a finite box without long range interactions and there is only a single bound state in the cavity. Both assumptions cannot be justified in any complete, coherent model.

In contrast to the extensive information available on the ground state and optical properties of the solvated electron very little is known concerning the dynamics of electronically excited states of excess electrons in polar solvents. The following indirect information concerning the fate of electronically excited states of the solvated electron in liquid ammonia is currently available. First, the band maximum in emission spectrum, which originates from a relaxed equilibrium $2p$ state to a $1s$ level in the same nuclear configuration, is distinctly red shifted from 0.9 eV in absorption to ~0.5 eV in emission,[9] since the equilibrium $2p$ charge density is rather diffuse. Second, no observation[12] of any fluorescence from the excited state of the solvated electron in liquid NH_3 was ever recorded, so that the nonradiative relaxation of the bound excited $2p$ state occurs on a time scale τ, which is short relative to the pure radiative lifetime τ_r, i.e., $\tau < 10^{-2}\, \tau_r$. As τ_r is expected to be $\sim 10^{-9}$ sec, as estimated from the transition moment for the $2p \rightarrow 1s$ transition, we expect that $\tau \lesssim 10^{-11}$ sec. In this context direct dynamical information regarding nonradiative relaxation processes in electronically excited states of the solvated electron in ammonia is desirable because of the following reasons:

(a) It is not known whether the broadening of the 1.5 μ absorption band originates from homogeneous phonon broadening together with the contribution of higher excited states, or alternatively inhomogeneous broadening effects may be operative. If homogeneous broadening prevails the entire spectrum should be proportionally bleached by optical pumping with a narrow ($\Delta\nu \sim 100$ cm^{-1}) band about $\nu^{-1} = 9431$ cm^{-1}, as employed in the present experiments. Evidence for "hole burning" in the trapped electron absorption band in methyltetrahydrofuran and 3-methylpentane glasses has been recently reported.[13] It is questionable whether such effects will be encountered in liquids.

(b) The nature of the nonradiative relaxation phenomena of the electronically excited states of the solvated electron is of considerable interest. The following possibilities should be considered in this context:

(1) The absorption band originates from the bound–bound $1s \rightarrow 2p$ transition in the nuclear ground state

configuration. The nuclear configuration in the excited state relaxes to the equilibrium $\overline{2p}$ configuration which in turn crosses to the ground state.[9] Such motion on potential surfaces corresponds to multiphonon nonradiative relaxation of the electron trapping center. One can also argue that the 2*s* excited state, which is characterized by a long radiative lifetime is involved. Theoretical calculations by Logan and Kestner[10] seem to rule out this possibility as the 2*s* state is located above the 2*p* state, due to the non-Coulombic nature of the potential at short distances, so that the $2p \rightarrow 2s$ nonradiative excitation will require appreciable activation energy and thus will be a slow process.

(2) The $1s \rightarrow 2p$ transition is followed by thermal ionization of the excited state, resulting in a quasifree electron which subsequently is trapped to the localized ground state. The second step of localization of the free electron was previously studied in liquid water[14] and in liquid alcohols.[15,16] This process involves two steps: an ultrafast initial localization followed by dipole relaxation in the first solvation layer, the latter occurring on the time scale of the dielectric relaxation of the solvent.

(3) The optical excitation involves a bound continuum transition and the quasifree electron which is directly produced and is now trapped to form a localized ground state.

In the present work we report an experimental study of optical bleaching of dilute $Na-NH_3$, $Na-ND_3$ solutions utilizing the techniques of picosecond spectroscopy. The results provide pertinent information concerning the line broadening and the nature of relaxation processes in the excited state of the solvated electron in liquid NH_3.

II. EXPERIMENTAL PROCEDURES

Dilute (2×10^{-4} M) $Na-NH_3$-and $Na-ND_3$ solutions in 2 mm cell (optical density D = 1.3) at 1060 nm in the temperature range − 60 − 75 °C were excited with a single pulse from a Nd^{3+} glass laser at 1.06 μ and interrogated by a 20 psec, 6.7 psec, and 3.3 psec echelon in the range 1100–900 nm. The optical arrangement providing the picosecond bleaching and interrogating pulses is portrayed in Fig. 1. A Nd^{3+} glass oscillator (Brewster/Brewster rod dimensions ~7 in. long × 1/2 in. diam) was mode locked with Eastman Kodak 9860 saturable dye in a 1 cm cell, yielding 1.06 μ pulse trains with average width ~8 psec[12] and separation ~7 nsec. Mode locking was monitored with an ITT F 4000 S1 fast photodiode and Tektronix 519 oscilloscope. Single pulse extraction[17] was achieved with a Pockels cell situated between crossed Glan polarizers. A 21 kV spark gap triggered by the first few rejected mode-locked pulses supplied a ~4 nsec duration half-wave voltage to the Pockels cell. Amplification of the transmitted 1.06 μ single pulse was provided by two Brewster/Brewster Nd^{3+} glass amplifiers with a measured total gain of ~50. The energy of the single pulse was 75 ± 10 mJ/pulse.[18] A multilayer dielectric beamsplitter reflected ~45% of the beam. The remainder was focused into a 20 cm path length cell containing CCl_4 where self-phase modulation[19] of the laser fundamental and stimulated Stokes Raman band at 1.13 μ produced a broadband continuum pulse[20] of duration comparable to the 1.06 pulse. This was split into an interrogating train of ten pulses separated by ~3.3, 6.7, or 20 psec using transmission echelon. The echelon train was focused into a point intersecting the excitation pulse in the $Na-NH_3$ sample cell. After passing through a McPherson 0.3 m monochromator (dispersion 53 Å/mm), each of the interrogating pulses

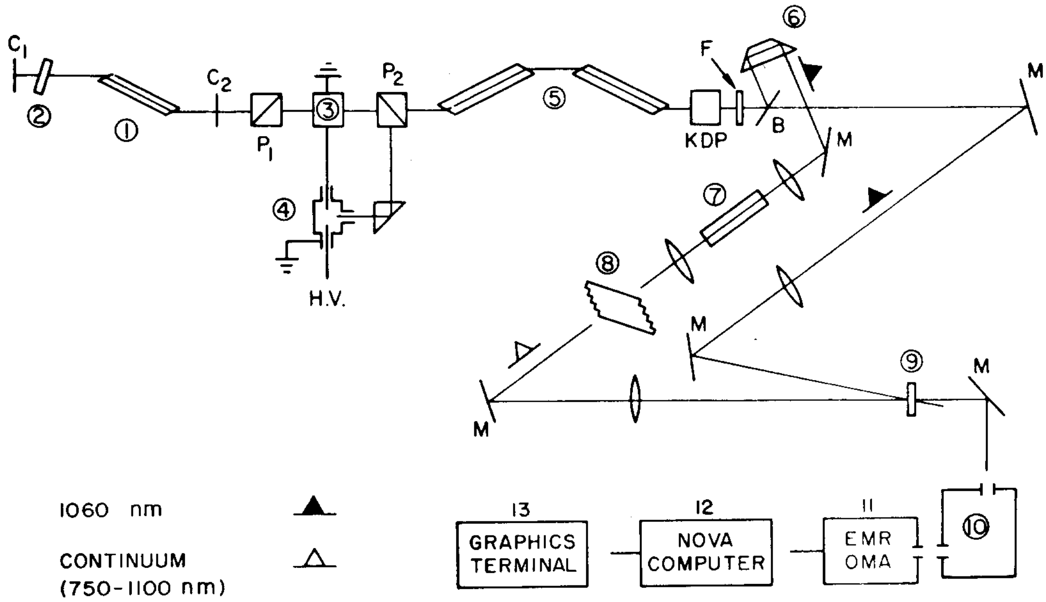

FIG. 1. Schematic representation of the experimental system. The components are the following (1) Nd^{3+} glass oscillator with cavity mirrors C_1, C_2; (2) saturable dye absorber cell; (3) Pockels cell positioned between crossed Glan polarizers P_1, P_2; (4) spark gap; (5) Nd^{3+} glass amplifiers; (6) translatable prism used to generate variable delay; (7) broad-band continuum cell containing CCl_4; (8) stepped-delay transmission echelon; (9) sample cell; (10) monochromator; (11) silicon vidicon optical data digitizer; (12) Nova computer; (13) graphics terminal. Mirrors are denoted by M, beam splitter B, optical filter F.

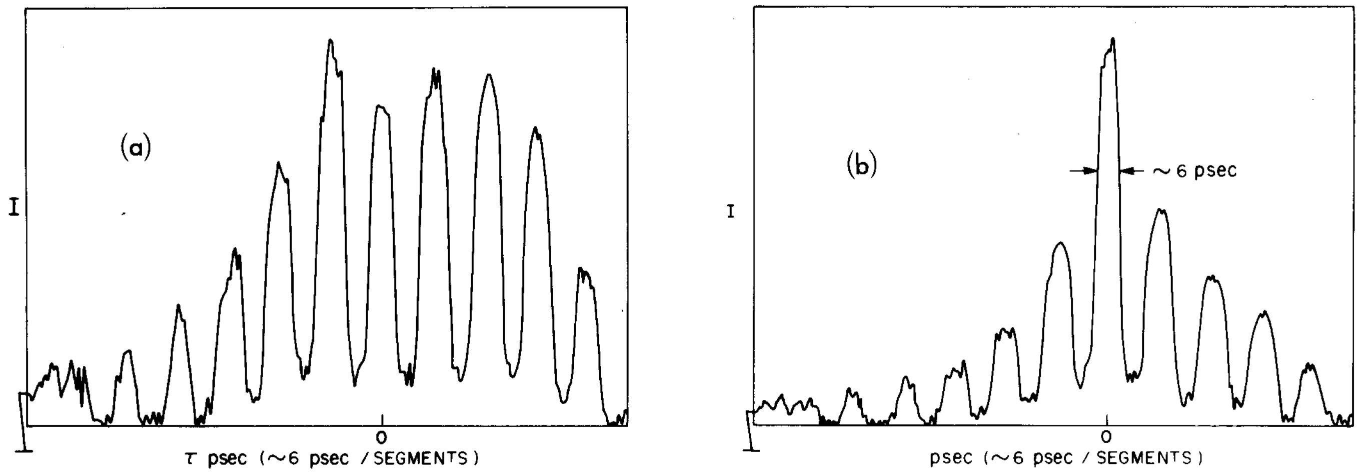

FIG. 2. Histogram of echelon pulses traversing through the ND_3/Na 2 mm cell. Intersegment separation 6 psec, wavelength 1100 nm, I designates relative transmitted intensity: (a) transmitted echelon segments without excitation; (b) same as (a) with excitation occurring at $t = 0$ segment.

was sharply imaged onto a distinct spatial region[21] onto an RCA 4532 silicon vidicon. The vidicon scan was controlled over a programmable two-dimensional grid by a Nova 1230 computer (Data General Corporation, Southboro, MA; interfacing electronics provided by EMR Photoelectric, Princeton, NJ). A LN_2 vidicon cooler (Products for Research, Danvers, Mass.) maintained the photocathode temperature at − 90 °C. Interrogating light intensities from each laser shot were stored by position (256×28 resolvable points were read from a thin, rectangular portion of the entire vidicon target for an accelerated readout) onto a moving-head disk file for further processing. These signals were integrated along the axis normal to the time coordinate to produce one-dimensional plots (Fig. 2) on a computer graphic therminal. Here, each sharply defined peak corresponds to a particular pulse in the interrogating train; these plots are similar to those produced by one-dimensional optical multichannel analyzers.

The synchronization of arrival of the 1.06 μ bleaching pulse and the $t = 0$ pulse in the interrogating train of pulses was verified by placing an Eastman Kodak 9860 dye solution (O.D. ~1.0 at 1.06 μ) in place of the sam-

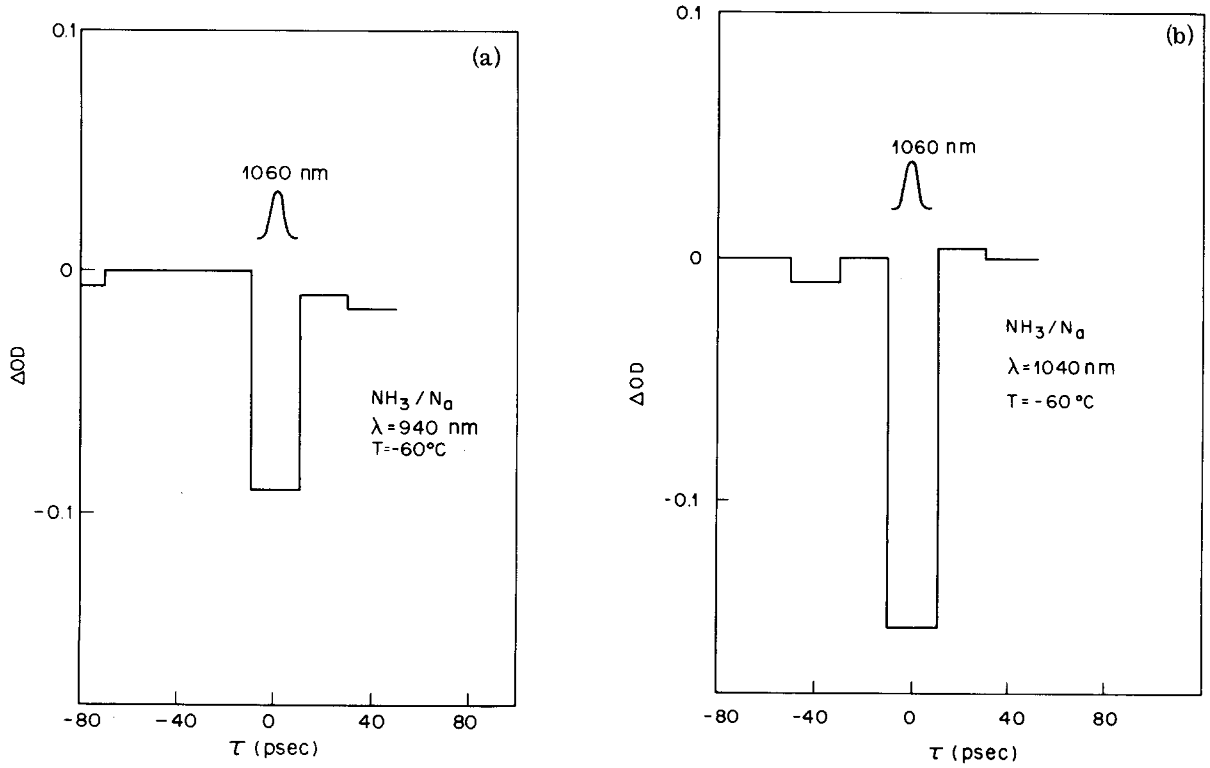

FIG. 3. Time resolved bleaching and recovery of the solvated electron absorption band of the sodium ammonia solution at (a) 940 nm, (b) 1040 nm. As shown the kinetic data is achieved by 20 psec echelon segments. The excitation was performed by a single 1.06 pulse generated by a mode locked Nd^{3+} glass laser.

ple. The relaxation time of this dye is ~6 psec. Quantitative bleaching of the saturable dye, lasting ~8–10 psec at 1.06 μ was achieved with unamplified 1.06 μ bleaching pulses (measured energy 2 mJ/pulse), but attenuation of these pumping pulses with neutral density filters[22] resulted in proportionate diminution of the bleaching O.D. change in the dye. As the extinction coefficient ($\epsilon \sim 5 \times 10^4$) and relaxation time (~6 psec) of the dye are independently known, these auxiliary experiments serve to calibrate bleaching intensities in $Na-NH_3$.

Alternate laser shots were taken with and without the bleaching (exciting) pulse entering the sample cell. Optical density changes were calculated for each echelon segment by evaluating $\Delta D = \log(I^w/I^n)$, where I^w and I^n refer to the intensity of the interrogating pulse in the presence and in the absence of the bleaching pulse, respectively. In the absence of the bleaching pulse the optical density changes between two different shots are small $\Delta D = \pm 0.03$, as compared to the values of $\Delta D \cong 0.3$ which were measured with the bleaching beam.

Bleaching of $Na-NH_3$ and $Na-ND_3$ solutions by a 25 mJ, 1.06 μ pulse was monitored in the spectral range 850–1100 nm, with a spectral resolution of 100 Å, using echelon time resolutions of 20 psec/segment, 6.7 psec/segment and 3.3 psec/segment. Typical experimental data for monitoring at 940, 1040, and 1100 nm are presented in Figs. 3 and 4. Over the whole spectral range which was monitored the bleaching and recovery take place within one echelon segment. The optical density changes at different wavelengths in the range 850–1100 nm are proportional to the absorption cross section of $Na-NH_3$ and $Na-ND_3$ solutions, as is evident from Fig. 5.

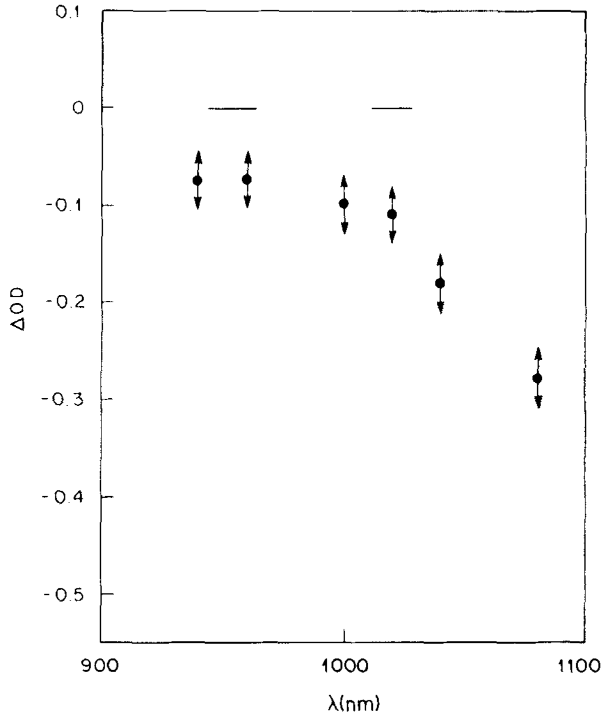

FIG. 5. Optical density changes (Δ O.D.) of the ammonia–Na absorption band as a function of wavelength (λ). The excitation was performed by a single 1060 nm pulse generated by a mode locked Nd^{3+} glass laser.

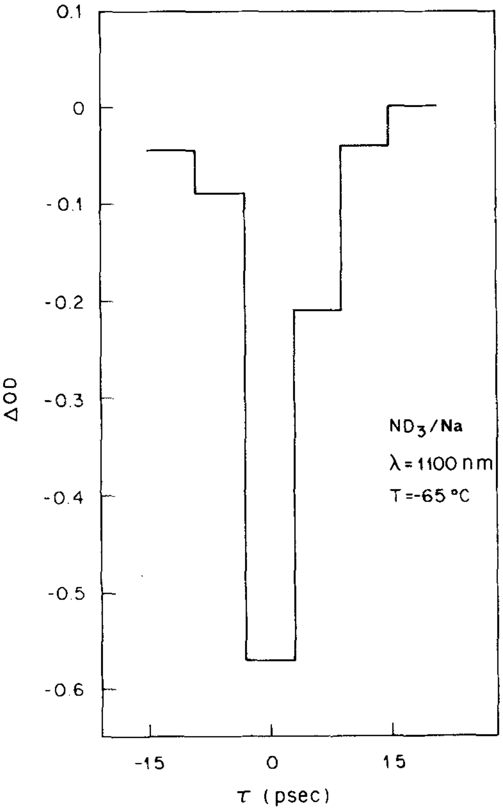

FIG. 4. Time resolved bleaching and recovery of the solvated electron absorption band of sodium deutrated ammonia solution at 1100 nm. In this case, the kinetics were monitored with 6.7 psec echelon/segments. All other experimental parameters same as Fig. 3.

Control experiments dispensing with the echelon and vidicon, but using exactly the same beam geometry[23] and employing an ITT F4000 S1 fast photodiode to detect reference and interrogating single pulses at 1.06 μ, yielded similar bleaching in $Na-NH_3$ for optimal synchronization of the pumping and interrogating pulses. This confirmed that the echelon technique yields results identical to those obtained with time consuming alternative methods.

III. SUMMARY OF EXPERIMENTAL RESULTS

The following experimental data were recorded for bleaching of dilute (2×10^{-4} M) $Na-NH_3$ solutions at −60 to −75 °C by a single 1,06 μ pulse (pulse length 8 psec and pulse energy 30 ± 10 mJ):

(a) Bleaching and recovery occurred within a single echelon segment, which in different experiments corresponds to time resolutions of 20, 6.7, and 3.3 psec.

(b) The shape of the interrogating pulse segments is symmetrical and identical before and after the bleaching. This lack of distortion of the interrogating pulse indicates that the bleaching and recovery are fast to an experimental time scale, i.e., the relaxation time τ exceeds the experimental time resolution by more than one order of magnitude, i.e., $\tau < 6 \times 10^{-13}$ sec.

TABLE I. Optical density changes (Δ O.D.) in NH_3/Na and ND_3/Na solution excited by a 1060 nm pulse and observed within the time of the pulse width.

λ (nm)	NH_3 Δ (O.D.)	ND_3 Δ (O.D.)
1100	···	0.44
1080	0.28	0.34
1040	0.18	0.21
1020	0.12	···
1000	0.10	0.17
960	0.09	···
940	0.08	···

(c) The bleaching by a 1.06 μ pulse with energy of 30 ± 10 mJ, subsequently monitored at 1100 nm with an echelon segment of 6.7 psec results in the optical density change of $\Delta D = 0.3 \pm 0.05$ for a solution characterized of optical density of $D_0 = 1.3$, so that $\Delta D/D = 0.23 \pm 0.05$. This result was utilized to evaluate the relaxation time, τ. Assuming that population of bound (or free) excited states does not contribute to optical absorption, one readily gets $\Delta D/D_0 = x/(1+x)$, where $x = \tau \epsilon l I$. Here $\epsilon = 2\times10^4$ M^{-1} cm^{-1} is the molar absorption coefficient, $l = 0.2$ cm the cell length and $I = 4\times10^{28}$ photon/cm^2 sec is the photon flux. Hence we estimate $\tau \cong 2\times10^{-13}$ sec for the regeneration of the ground state of the solvated electron in NH_3 at − 70 °C.

(d) The degree of bleaching at 1.06 μ monitored at each wavelength in the range 850–1100 nm follows the energy dependence of the absorption cross section of the solvated electron in liquid NH_3 and ND_3. A summary of the data is shown in Table I and Fig. 5.

IV. DISCUSSION

From our experimental data for the optical bleaching of the solvated electron absorption band in liquid ammonia two major conclusions emerge which pertain to the problem of the nature of the broadening of the absorption band and the relaxation processes in the excited state. First, we have demonstrated that pumping by a narrow band (~ 100 cm^{-1}) at 1.06 μ results in a proportional bleaching in the range 1100–850 nm so that the broad absorption band of the solvated electron in liquid NH_3 (at least in the energy range 1.11–1.46 eV) is homogeneously broadened. After excluding the possibility of inhomogeneous broadening of the solvated electron absorption band, on experimental grounds the theory of phonon type broadening of the $1s - 2p$ and the higher $1s \rightarrow np$ transitions[9] has to be refined to account for the observed line broadening. Such a treatment should include the dependence of the transition moment and the nuclear configuration together with incorporation of the role of nontotally symmetric molecular distortions around the electron trapping center. Second, the ultrashort, subpicosecond relaxation time $\tau = 2\times10^{-13}$ sec for the excited state at − 70 °C provides us with the first direct, through still incomplete, information concerning the relaxation dynamics in this system. We cannot ascertain with complete confidence whether the bound–bound $1s \rightarrow 2p$ excitation is followed by "intramolecular type" relaxation between the bound $2p$ state to the ground state, or alternatively, whether a two step process involving thermal ionization of the excited state followed by trapping of the quasifree electron occurs. The trapping of the quasifree electron in polar solvents occurs in two stages: initial trapping due to relaxation of long range polar modes followed by local relaxation of the first coordination layer which proceeds as the time scale of dielectric relaxation.[14] Utilization of the techniques of picosecond spectroscopy to the study of the localization of quasifree electrons in H_2O at 300 °K resulted in a lifetime of 0.5 psec for the initial stage[14] and 4 psec for the lifetime of the second stage,[14] while pulse radiolysis studies[15,16] led to lifetimes of 2.2 psec in CH_3OH at 300 °K, 10 psec in C_2H_5OH at 300 °K and ~ 2 psec for H_2O at 236 °K for the second stage of the evolution of the entire equilibrium type spectrum of the solvated electron. Our relaxation time for solvated electrons in NH_3, $\tau \cong 2\times10^{-13}$ sec at 203 °K is considerably shorter than these values[14–16] for CH_3OH and H_2O. We thus infer that excitation of the $1s - 2p$ transition of the solvated electron NH_3 results in "intramolecular type" nonradiative relaxation to the ground state, without the involvement of thermal ionization to an intermediate quasifree electron state. To establish conclusively this point, independent studies of the localization of the quasifree electron in liquid ammonia are required, which should proceed on a time scale which is longer than the relaxation of the $2p$ state.

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[1] *Metal Ammonia Solutions*, edited by G. Lepoutre and M. J. Sienko (Benjamin, New York, 1964).

[2] *Metal Ammonia Solutions*, edited by J. J. Lagowski and M. J. Sienko (Butterworth, London, 1970).

[3] *Electrons in Fluids*, Proceedings of Colloque Weyl III on Metal-Ammonia Solutions, edited by J. Jortner and N. R. Kestner (Springer–Verlag, Heidelberg, 1973).

[4] M. H. Coehn and J. C. Thompson, Adv. Phys. **17**, 857 (1968).

[5] J. Jortner, J. Chem. Phys. **30**, 839 (1959).

[6] R. H. Land and D. E. O'Reilly, J. Chem. Phys. **46**, 4496 (1967).

[7] D. A. Copeland, N. R. Kestner, and J. Jortner, J. Chem. Phys. **53**, 1189 (1970).

[8] A. Gaathon and J. Jortner, see Ref. 3, p. 429.

[9] N. R. Kestner and J. Jortner, J. Phys. Chem. **77**, 1040 (1973).

[10] J. Logan and N. R. Kestner, J. Phys. Chem. **76**, 2738 (1972).

[11] T. Kajiwara, K. Fanabashi, and C. Nalewg, Phys. Rev. **6**, 808 (1972); K. Fanabashi, *Advances in Radiation Chemistry*, edited by M. Rubton and J. L. Magee (Wiley, New York, 1974), Vol. 4, p. 103.

[12] We are not aware of any negative published report in the literature concerning this point, however research for emission was performed by several groups without any positive results.

[13] S. L. Hager and J. E. Willard, paper presented at the Atlantic City A. C. S. meeting, September 1974, (unpublished).

[14] P. M. Rentzepis, R. P. Jones, and J. Jortner, J. Chem. Phys. **59**, 9 (1973).

[15] L. Gilles, J. E. Aldrich, and J. W. Hunt, Nature (Lond.) Phys. Sci. **243**, 70 (1973).

[16] J. H. Baxendale and P. Wardman, J. Chem. Soc. Faraday Trans. T **69**, 584 (1973).

[17] T. L. Netzel, W. S. Struve, and P. M. Rentzepis, Annu. Rev.

Phys. Chem. **24**, 473 (1973).

[18] Determined using a Hadron model 100 ballistic thermopile.

[19] F. Shimizu, IBM J. Res. Dev. **17**, 286 (1973); and references cited therein.

[20] C. G. Varma and P. M. Rentzepis, J. Chem. Phys. **58**, 5237 (1973); M. Clerc, R. P. Jonse, and P. M. Rentzepis, Chem. Phys. Lett. **26**, 167 (1974).

[21] A cw Nd^{3+}:YAG laser was used for alignment and focusing of the echelon images.

[22] Care was taken to select filters immune to detectable bleaching by the present 1060 nm pulse energies (up to ~100 mJ when amplified).

[23] The interrogating pulses were focused to ~1 mm diameter, in the center of the sample cell; the bleaching pulse was condensed to ~4 mm diameter; and the intersection angle (exaggerated in Fig. 1 for clarity) was $< 10°$.