Structure in the Optical Absorption Spectrum
of the Solvated Electron? *

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Abstract

The optical absorption spectrum of the solvated electron in ethanol has been determined again to establish whether a report of observed structural features by Vannikov and Marevtsev, which appears to be discordant with earlier data, can be sustained. Our data do not reveal such structural features, and are furthermore in significant disagreement with the general contour of the absorption band reported by these authors.

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Introduction

The optical absorption spectrum of the solvated electron in liquids has generally been reported as a broad, structureless band.¹⁻⁶ The question of whether this band is composed of several narrower bands representing transitions between quantized energy states is of theoretical⁷⁻⁹ interest. For a purely continuum model, there has been speculation as to whether bands of the nature of a Rydberg series may exist. For a cavity model,^{9,10} in which short range interactions are important, there may conceivably be structure related to molecular properties of the near neighbors of the solvated electron.

This question of structure may be viewed from two aspects:

(a) whether the smooth, structureless band may be deconvoluted mathematically into separate, overlapping bands, as suggested by Delahay,¹¹ to represent bound-bound and bound-continuum transitions, or (b) whether structure may indeed be observable if the wavelength resolution and reproducibility of optical density measurements are sufficient. It is the latter aspect only, of this question, to which this paper is directed.

Observable structure in the optical absorption spectrum of e_s^- in ethanol has recently been reported by Vannikov and Marevtsev.¹² Their observations do not seem to be in accord with earlier data^{3,4} for e_s^- .

in the alcohols. It is possible that this recent observation of structure is the result of improvements in technique. We have, therefore, carefully repeated the observations for ethanol, accumulating a rather large mass of data. Our data do not support the claim¹² that structure is observable in the form of four separate peaks, over the wavelength region 680 to 820 nm.

Experimental

The source of the electron pulse, as in earlier work,¹³ was a Varian V-7715A electron linear accelerator. In this investigation, 400 ns pulses of 3-4 MeV electrons, with a beam current of about 325 mA, were used. Such pulses deliver a dose of about 2.4×10^{17} eV/g. The irradiation cells were made of fused quartz, with optical windows of high purity silica, and were 20.0 mm long in the direction of the analyzing light beam. A double pass was used giving a 40.0 mm optical path through the cell. Each cell was connected to a 50 ml Pyrex storage bulb. The bulbs were equipped with Teflon stopcocks and Teflon-seal joints to allow connection to a vacuum system.

The scatter of repeated optical density measurements would normally depend upon pulse reproducibility, which in our case is approximately $\pm 3\%$. This source of error was eliminated by splitting the analyzing light beam into two parts with the use of a partially transmitting mirror, so that the transient absorption could be observed at two wavelengths simultaneously. Thus, one wavelength could remain fixed while the other was varied. The fixed wavelength, 500 nm in this case, was used as a reference standard to normalize any variations in pulse intensity and thus to improve the reproducibility of the optical density measurements. Bausch and Lomb grating monochromators,

Type 33-86-25, $f/3.5$, were used with three different gratings of the following wavelength ranges and reciprocal dispersions: 350-800 nm, 6.4 nm/mm; 200-700 nm, 7.4 nm/mm; 700-1600 nm, 12.8 nm/mm. Monochromator entrance and exit slits were always set to give a band pass of 3.6 nm. Appropriate Corning glass filters were placed in the optical path before the cell to prevent photolysis of the sample, and in front of the monochromators to eliminate second-order diffraction effects.

RCA photomultiplier tubes 7102 and 7200, having S-1 and S-19 spectral responses, respectively, were used to monitor the optical absorption. These photomultiplier tubes were coupled, through an amplifier system with a 70 ns risetime (for 10 to 90%), to a dual-beam oscilloscope. Polaroid photographs of the rate curves were enlarged by a factor of three before measurements were made of the traces on them.

Absolute ethyl alcohol, U.S.P., was obtained from Commercial Solvents Corporation, Terre Haute, Indiana, U.S.A. The ethanol was distilled under argon at one atmosphere, first from an acidic 2,4-dinitrophenylhydrazine solution, and then from a sodium ethoxide solution. The purified ethanol was degassed immediately after collection (three freeze-pump-thaw cycles) and stored under vacuum in the dark until needed.

The spectrum reported here is a composite of repeated results obtained from the irradiation of four separate samples. Samples were prepared by vacuum distillation of from 35 to 40 ml of ethanol into each

of the Pyrex storage bulbs. After each electron pulse, the irradiated ethanol was mixed with that in the storage bulb to give a 20-fold dilution of any stable radiolysis products that may have been formed. No sample was ever subjected to more than 60 pulses, and over the course of any experiment no change was perceptible in either the yield or the decay kinetics of e_s^- as monitored at the fixed wavelength of 500 nm. The spectral region 630 to 770 nm was covered once with each of the four samples and twice with two of them. With two of the samples the entire 500 to 900 nm region was covered.

Results and Discussion

The purpose of this investigation is to ascertain whether the structure in the room temperature spectrum of e_s^- in ethanol shown in the paper of Vannikov and Marevtsev,¹² and again in a current report¹⁴ from their laboratory, which a reviewer has kindly brought to our attention, is indeed real. Two characteristics of our measurement capability are important: (1) the scatter in the amplitude of the optical density measurements at any given wavelength, compared with the magnitude of the difference between structure-determining points in their paper,¹² and (2) the bandpass used in our measurements compared with the width of the reported structural features. The maximum spread in our optical density measurements at any wavelength (see Fig. 2) over the region 650 to 850 nm is $\pm 2.2\%$; the average deviation from the mean at any wavelength is about $\pm 1.3\%$. Since the structural features reported by Vannikov and Marevtsev show a spread of 3.5% at 680 nm, and only slightly less at other wavelengths,¹² and, indeed, an even greater spread, exceeding 10% at another wavelength in their more recent paper,¹⁴ our measurements should reveal these features. The bandpass we have used

is 3.6 nm, rather better than the bandpass of 9 to 15 nm which we infer from the literature¹⁵ was used by Vannikov and Marevtsev¹² in their first report, and at least comparable to the resolution of 2.5 to 6.0 nm which they have indicated more recently.¹⁴ A bandpass of 3.6 nm should be adequate for measurement of the reported structural features which exhibit a width at half-height of about 16 nm.

Shown in Fig. 1 is the spectrum of e_s^- in ethanol that we have obtained. Each point is an average of from 2 to 7 repeated determinations. The smooth curve passing through the points we believe best fits the data. The curve reported by Vannikov and Marevtsev¹² has been included in Fig. 1 for comparison. Clearly, their curve does not fit our data well. The discrepancy is particularly apparent in the decline of their optical density from 680 nm to a structural minimum at 700 nm, and in the rise to a peak at 820 nm. In both cases this discrepancy is some two-fold larger than the uncertainty in our measurements, which thus do not sustain their report of observed structure. Moreover, comparison of the spectrum reported in the recent work¹⁴ with the earlier data¹² indicates an inconsistency in both the amplitude of some peaks and valleys in the reported structure,^{12,14} as well as opposite shifts in the wavelength of two peaks. These authors have commented¹⁴ upon such variations and have attributed them to differences in the individual alcohol samples.

Perhaps some understanding of the problem in defining such structure may be obtained from Fig. 2. Each point in Fig. 2 represents an optical density measurement made after a separate electron pulse. The scatter in these points at any given wavelength reflects the uncertainty in the measurement of the transient absorption.

The deviations of our data points from the smooth curve which has been drawn through them in Fig. 1 are all less than our uncertainty of about $\pm 1.3\%$. A smooth curve without structural features thus seems to be called for by the data.

A separate but not totally unrelated question arises regarding the disagreement of our data with the spectrum of Vannikov and Marevtsev at wavelengths shorter than 600 nm and longer than 820 nm. Contrary to their assertion¹² that their data are in agreement with the general contour line of the spectrum in earlier work,³ there seems to be substantial disagreement at the longer and particularly at the shorter wavelengths. Their disagreement is not only with the earlier work,³ but also with our present repetition of these measurements as well as with a recent set of data of Jha et al.¹⁶ All four sets of data are shown in Fig. 3.

Acknowledgment

It is an honour to participate in this memorial issue dedicated to Professor Robert L. Platzman. The intellectual stimulation and the guidance he provided to our work on solvated electrons as well as to other areas of our research, over the past decade, has been of profound importance to us.

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Figure Legends

Fig. 1. Optical absorption spectrum of the solvated electron in ethanol at 296°K. The open circles represent our experimental data, each point being the average of two to seven individual data points. The dashed line represents the data of Vannikov and Marevtsev normalized to our data at 680 nm.

Fig. 2. Optical absorption spectrum of the solvated electron in ethanol at 296°K showing each individual data point obtained in the present investigation.

Fig. 3. Optical absorption spectrum of the solvated electron in ethanol at room temperature obtained by different authors. ——— Sauer, Arai and Dorfman, ref. (3); ——— Gavlas and Dorfman, present investigation; ——— Jha, Bolton, and Freeman ref. (16); ——— Vannikov and Marevtsev, ref. (12).

FIG. 1 GAULIN & DOREMAN

FIG. 2. CHALOS & DOREMAN.

FIG. 3. GAULAS + DOREMAN.