with acetonitrile; the electronic spectrum and chemical characteristics of such solutions have been recorded.[1a] Since acetonitrile forms a stable complex with Cu(I),[6] dissolution of **1** in acetonitrile should occur with the formation of $(CH_3CN)_4Cu^+$ and the liberation of the phenyldiazene. This, in fact, does occur. Dissolution of **1** in acetonitrile under the rigorous exclusion of molecular oxygen followed by careful distillation of the solution under the conditions described in ref 1a yields a solution of phenyldiazene as evidenced by its electronic spectrum (λ_{max} 417, 260, 215 nm) and by the rapid change in this spectrum upon exposure of the solution to molecular oxygen.

Stabilization of phenyldiazene in these complexes is probably due to simple physical isolation of the diazene, so that its reaction with other reagents, including itself, is inhibited. Attempts to prepare similar complexes of methyldiazene and benzyldiazene have been unsuccessful, although the reduction of Cu(II) to Cu(I) can be effected by both of the corresponding hydrazines. Steric factors may account for the failure to isolate complexes in these cases, since it is imperative that a suitable, stable lattice be formed to trap the diazene. A stable diazene complex has been formed from the reaction of cupric chloride with 1,1-dimethylhydrazine. This complex is characterized by a lack of any N–H stretching vibration in the infrared spectrum and the presence of an N=N stretching vibration at 1550 cm^{-1}. The infrared spectrum of this new complex is different from that of $(CH_3N{=}NCH_3)Cu_2Cl_2$, which does not exhibit an infrared-active N=N stretching frequency.[5] Treatment of the complex derived from 1,1-dimethylhydrazine with hydrochloric acid followed by neutralization yields tetramethyltetrazene, $(CH_3)_2NN{=}NN(CH_3)_2$, in good yield. Although these results suggest that dimethyldiazene is not present in the complex; the coordinated species could be either 1,1-dimethyldiazene,[7] $(CH_3)_2N^+{=}N^-$, or its dimer, tetramethyltetrazene.[8] Experiments designed to differentiate between these two possibilities are in progress.

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[6] B. J. Hathaway, D. G. Holah, and J. D. Postlethwaite, *J. Chem. Soc.*, 3215 (1961).

[7] W. R. McBride and H. W. Kruse, *J. Amer. Chem. Soc.*, **79**, 572 (1957).

[8] Isolation of tetramethyltetrazene from the complex after acidification and subsequent neutralization does not establish the presence of the tetrazene in the complex, since neutralization of acidic solutions thought to contain 1,1-dimethyldiazene is known to produce tetramethyltetrazene.[7]

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Vibrational Structure in the Electronic Absorption Spectrum of the Trapped Electron in Crystalline Acetonitrile-d_3 at 77°K[1]

Sir:

Solvated and trapped electrons are invariably characterized by a broad optical absorption in the visible or near-infrared. The nature of this electronic transition has been widely discussed for several different systems,[2] but progress has been hindered by the absence of any resolved structure in the band. In this communication, we report the discovery of vibrational fine structure in the optical absorption spectrum of a trapped electron in molecular crystals of acetonitrile-d_3. It is well known[3] that the electronic absorption spectra of molecules in crystals frequently show vibrational structure, especially at low temperatures.

We know from esr studies[4–8] that trapped electrons are produced in samples of crystalline acetonitrile-d_3 by γ irradiation at 77°K. The esr hyperfine structure of this paramagnetic species in quenched crystals is a quintet for the ^{14}N compound[4–6] and a triplet for the ^{15}N compound,[7] so it has been definitely established that the trapped electron interacts magnetically with two (and only two[8]) equivalent nitrogen nuclei. On photobleaching the sample with visible light at temperatures between 77 and 113°K, the esr spectrum of the trapped electron is replaced by the septet spectrum of $CD_3\cdot$. This change has been interpreted[4] as the *net* effect of dissociative electron capture. If the photobleached sample is kept in the dark, the reverse overall reaction occurs and the trapped electron is regenerated quantitatively at a rate which depends on the temperature. The activation energy for thermal recovery[8] is 4.6 kcal mole^{-1}.

The presence of a trapped electron in γ-irradiated acetonitrile-d_3 is indicated also by an optical absorption with λ_{max} at 510 nm. That the esr and optical absorption spectra refer to the same center has now been proved unequivocally by experiments showing that the optical spectrum is also restored thermally after photobleaching without any loss of intensity for the complete cycle.

Figure 1 shows the fine structure in the optical spectrum taken before photobleaching. The possibility that the undulations represent some artifact of the experimental optics is ruled out by the total disappearance of this structure in the spectrum recorded immediately after the sample had been photobleached *in situ* without change of cell position or other experimental conditions. Moreover, from a comparison of the spectra recorded in several different experiments using cells of different construction with two spectrophotometers, it is found that the positions of the peaks and troughs are exactly reproducible, and this fine structure is regained with perfect fidelity on thermal recovery after photobleaching.

Inspection of the entire spectrum reveals a long progression of more than 40 bands originating at 1.151×10^4 cm^{-1} with a mean separation of 306 cm^{-1}. This spacing is virtually constant within the precision of our measurements, although there appears to be a slight trend from 309 to 303 cm^{-1} over the entire absorption in the direction of increasing frequency, as deduced

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[1] This work was supported by the U. S. Atomic Energy Commission under Contract No. AT-(40-1)-2968. This is AEC Document No. ORO-2968-50.

[2] For references, see J. Jortner and S. A. Rice, Advances in Chemistry Series, No. 50, American Chemical Society, Washington, D. C., 1965, p 7.

[3] D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals," Academic Press, New York, N. Y., 1959, p 24 ff.

[4] M. A. Bonin, K. Tsuji, and F. Williams, *Nature*, **218**, 946 (1968).

[5] M. A. Bonin, K. Takeda, and F. Williams, *J. Chem. Phys.*, **50**, 5423 (1969).

[6] K. Takeda and F. Williams, *Mol. Phys.*, 17, 677 (1969).

[7] K. Takeda and F. Williams, unpublished work.

[8] M. A. Bonin, Ph.D. Thesis, The University of Tennessee, 1969.

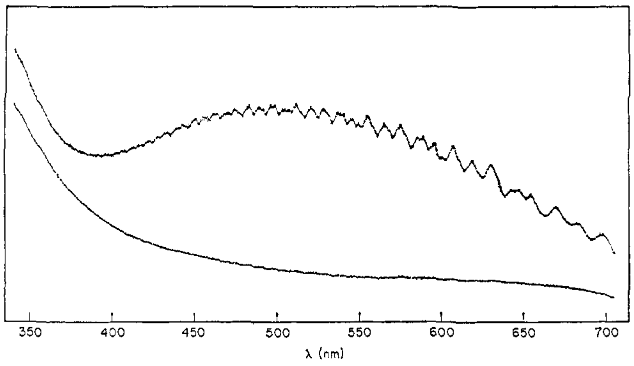

Figure 1. The absorption spectrum of γ-irradiated crystalline acetonitrile-d_3 at 77°K. Upper and lower spectra were recorded before and after photobleaching with visible light from the IR2 lamp of the Cary 14 spectrophotometer. The thickness of the optical cell was 0.1 cm and the γ-irradiation dose was 1 Mrad (6.2×10^{19} eV g^{-1}). The ordinate refers to a linear optical density scale such that the difference between the two curves at 510 nm is 0.65. That portion of the spectrum which lies beyond 700 nm is not shown, since it could not be recorded with the Cary 14 spectrophotometer used in this experiment because of the sensitivity of the absorption band to photobleaching by the IR2 lamp. The red portion of the spectrum was recorded in separate experiments using a Cary 14R instrument.

from separations averaged over several successive bands. At the beginning of the progression there seems to be marked intensity alternation such that one or two bands are too weak to be clearly resolved. On the high energy side of the absorption envelope, the structure is ultimately lost in the region of 2.50×10^4 cm^{-1}. While the existence of overlapping progressions is not revealed in the present spectra, this possibility should not be excluded and a complete analysis must await the better resolution which should be obtainable at 4°K.

The magnitude of the observed separation (306 cm^{-1}) leaves little doubt that this frequency is associated with a bending vibration in the upper state. For neutral CD_3CN in the ground state, the C—C≡N bending frequency is 331 cm^{-1} as determined from infrared studies.[9] The existence of a long progression in the bending mode is frequently characteristic of a transition from a linear ground state of the molecule to a bent upper state.[10] Therefore, we infer that in the present case, the electronic transition involves the promotion of the electron, which is trapped between two CD_3CN molecules, to a vacant molecular orbital (probably π^*) of CD_3CN, thereby forming a negative ion which assumes a bent structure in its equilibrium conformation. This negative ion may be formed in an electronically excited state. Since the esr studies show that photobleaching in this absorption band leads to the formation of $CD_3\cdot$, it is likely that predissociation occurs in this upper state. A schematic representation of the paths for photobleaching and thermal recovery in terms of potential energy curves has been given elsewhere.[8]

Vibrational fine structure has also been clearly observed in the corresponding absorption spectrum of the trapped electron in acetonitrile-h_3, and a detailed comparison of this structure with that produced in CD_3CN is now in progress. We plan to extend this work to include acetonitrile-d_1 and acetonitrile-d_2. As reported previously,[4] the trapped electron in CH_3CN is not recovered after photobleaching.

It is impossible, of course, to generalize from the present observations for this rather well-defined system to the nature of the optical transition for solvated and trapped electrons in other molecular assemblies. However, this work does suggest that the upper state can be the negative ion of a solvent molecule instead of being considered as an excited state of the solvated or trapped electron in the potential energy well of the surrounding molecules.[2]

A fuller account of our studies[11] will be reported in due course.

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(9) W. H. Fletcher and C. S. Shoup, *J. Mol. Spectrosc.*, 10, 300 (1963).

(10) G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. III, D. Van Nostrand Co., Inc., Princeton, N. J., 1966, p 167 ff.

(11) This contribution is based on work to be described in the M.S. Thesis of L. Holloman, The University of Tennessee, 1970.

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Reference-Independent Nuclear Magnetic Resonance Solvent Shifts

Sir:

We introduce here a reference-independent nuclear magnetic resonance (nmr) solvent shift and report data for converting measurements made with either internal or external references to the new scale. Use of this scale avoids the uncertainties inherent in the usual procedure of reporting nmr solvent shifts relative to a necessarily arbitrary reference solute. To obtain reference-independent solvent shifts to the desired accuracy (0.01 ppm) it is essential to determine accurately the bulk susceptibility difference between the two solvents involved. This has been accomplished by devising a new technique for measuring the bulk susceptibility difference, which yields values considerably more accurate (by at least an order of magnitude) than are available by subtraction of published susceptibility values.

In measuring proton magnetic resonance solvent shifts as an aid to molecular structure determination,[1–4] it has become customary to use an internal reference (usually tetramethylsilane, TMS) in both solutions, and to express the results for the solute protons as shifts in their resonance positions relative to the reference peak. In the usual notation, such a solvent shift is defined as

$$\Delta_y{}^x = \delta(y) - \delta(x) \qquad (1)$$

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(1) P. Laszlo, "Progress in Nuclear Magnetic Resonance Spectroscopy," Vol. 3, J. W. Emsley, J. Feeney, and L. H. Sutcliffe, Ed., Pergamon Press, Oxford, 1967.

(2) J. V. Hatton and R. E. Richards, *Mol. Phys.*, 5, 139 (1962).

(3) J. Ronayne and D. H. Williams, *J. Chem. Soc.*, *C*, 2642 (1967).

(4) T. Ledaal, *Tetrahedron Lett.*, 1683 (1968).