Infrared Spectroscopy of [$^2H_8$]Naphthalene in its Lowest Triplet State

By RICHARD H. CLARKE,* PHYLLIS A. KOSEN, MARIAN A. LOWE, RICHARD H. MANN, and RICHARD MUSHLIN
(Department of Chemistry, Boston University, Boston, Massachusetts 02215)

Summary An i.r. absorption band found at 535 cm^{-1} corresponds to an absorption in the photoexcited triplet state of the [$^2H_8$]naphthalene molecule.

WE have begun an i.r. investigation of organic molecules excited into their lowest triplet state. The long lifetime of the triplet state allows build-up of sufficient steady state population to make i.r. spectroscopy possible in the excited state. Such an experiment has been reported on a system containing [$^2H_8$]naphthalene by Hexter without attempting to assign or verify the origin of the light-dependent signals observed.[1] We report the first results of excited state i.r. spectroscopy on the triplet state of the system [$^2H_8$]-naphthalene in a Nujol solution at *ca.* 80 K. The experiments were performed using a Perkin Elmer model 180 spectrometer. The sample was positioned in the spectrometer beam in a low temperature cell which allowed simultaneous illumination of the sample through a quartz side window by a 200 W Hg high-pressure u.v. lamp.

With the u.v. lamp focused on the sample a new peak at 535 cm^{-1} appeared in the i.r. spectrum. The peak disappeared when the u.v. lamp was shuttered and decayed with a lifetime of $\tau_{\mathrm{i.r.}}$ 20·6 ± 1·2 s. A measurement of the phosphorescence decay of the [$^2H_8$]naphthalene in Nujol at 77 K gave a lifetime of τ_{p} 20·4 ± 2·4 s. In addition the known e.s.r. spectrum of the photoexcited triplet state of [$^2H_8$]naphthalene in Nujol was obtained at 77 K. The $\Delta m = 2$ e.s.r. signal decayed with a lifetime of $\tau_{\mathrm{e.s.r.}}$ 19·8 ± 0·7 s. Both the phosphorescence and e.s.r. decay times are in good agreement with triplet lifetimes reported for [$^2H_8$]naphthalene in various matrices.[2] The consistency (within experimental error) of the decay times from these three experiments for the [$^2H_8$]naphthalene in Nujol system implies that the u.v. light-dependent absorption observed in the i.r. spectrum (Figure) originates in the lowest triplet state of the [$^2H_8$]naphthalene molecule.

The strongest absorption band in the ground state i.r. spectrum of [$^2H_8$]naphthalene in Nujol occurs at 630 cm^{-1} (see Figure). This band is assigned as a b_{3u} out-of-plane mode.[3] It would seem reasonable to consider the 535 cm^{-1} transition to be the same b_{3u} normal mode in the excited state. This assignment is consistent with several points known about the naphthalene triplet state. First, one would expect vibrational frequencies from 400—1000 cm^{-1} involving ring motions[3,4] to be reduced in the excited triplet state (less bonding character in the π electron system due to promotion of an electron to an antibonding orbital). Also, the reduction in excited vibrational frequency of 95 cm^{-1} agrees with the reduction of low frequency vibrations found in the singlet-triplet absorption spectrum of the naphthalene crystal.[5] Further, if the geometry in the excited state is not grossly different from that found in the ground state, as is suggested in our e.s.r. experiments, then one might expect the excited state b_{3u} mode associated with the 630 cm^{-1} ground state normal mode to be the strongest band in the light-dependent i.r. spectrum. From the reduction in intensity of the ground state i.r. peaks on illuminating the sample with the u.v. exciting light we estimate our steady state excited state population to be *ca.* 2% of the [$^2H_8$]naphthalene molecules on the sample. A more efficient optical pumping source leading to a larger excited state population is required to observe additional triplet state vibrational frequencies to substantiate such tentative assignments.

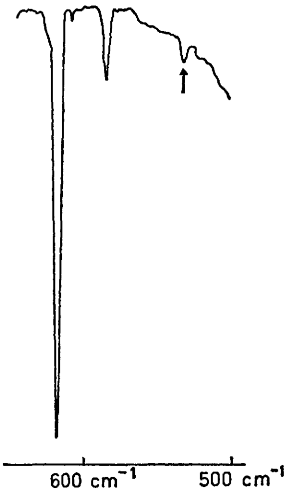

FIGURE. *Portion of the i.r. spectrum of photoexcited* [$^2H_8$]*naphthalene in Nujol at* 80 K. *Arrow indicates position of light-dependent absorption.*

We thank Dr. R. E. Connors for assistance with the esr experiments and the U.S. Army Research Office (Durham), the Research Corporation, the Petroleum Research Fund administered by the American Chemical Society, and the Alfred P. Sloan Foundation for support.

(*Received*, 21*st May* 1973; *Com.* 732.)

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