

magnitude of the non-lattice contribution to the atomic heat is concerned, Jones' theory^{1,2} is not in disagreement with our experimental results. The complexity of the model which Adams²² presents as an alternative to that of Jones makes a calculation of the expected

²² E. N. Adams II, *Phys. Rev.* **89**, 633 (1953).

carrier contribution to the heat capacity very difficult. Such a calculation might, however, offer a useful test of its applicability.

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Magnitude of Excitation Energy and Energy Transfer by Collision*

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Energy transfer by collision in fluorescent solutions is found to drop sharply when the excitation energy of the solute molecule is very close to or below that of the transferring molecule. The results indicate that energy is transferred only when molecules are close to each other as in collision.

HIGH-ENERGY-INDUCED fluorescence in liquid solutions has been shown to be associated with a transfer of energy from an excited solvent molecule to a solute molecule.^{1,2} We are now reporting a special instance where such energy transfer takes place between added naphthalene and various solute molecules. Naphthalene is a solid at room temperature, but it can effectively be used as a solvent for high-energy fluorescence by dissolving large amounts of it in a solvent which may by itself have only mediocre ability to transfer energy. About 300 grams per liter of naphthalene in *n*-butylphosphate is such a system.³ Various highly efficient solutes (in xylene) such as α, α' -binaphthyl, 2, 5-diphenyloxazole and 9, 10-diphenylanthracene were studied in this "solvent" combination. The energy transfer to the solute takes place almost exclusively from the excited naphthalene molecules; such a "solvent" combination is found to be almost as effective as xylene for the solutes mentioned. *p*- and *m*-terphenyl behave quite differently; when these substances are put into this "solvent" combination, only small fluorescence occurs, although in xylene both of these materials are highly efficient. This result is interpreted by assuming that no energy transfer takes place from naphthalene to *p*- or *m*-terphenyl. If one of these latter molecules is added to a fluorescent solution containing one of the above-mentioned solute molecules, the light output is scarcely changed. This result can be interpreted in the same way.

The explanation proposed here for this behavior is based on the assumption that the energy jump from the ground state to the first singlet state in the ter-

phenyls is slightly too great to enable frequent transfer from naphthalene. Judging by the published absorption curves of naphthalene and *m*- and *p*-terphenyl one can only say that their lowest excited states are very close.⁴ α, α' -binaphthyl, to which a very good energy transfer occurs in this "solvent" combination, also has an absorption edge close to that of naphthalene. From the absorption curves, one concludes that the lowest excitation energy for α, α' -binaphthyl probably does not differ by more than 1/10 of an electron volt from the respective excitation energy of naphthalene.

The difference in behavior between the terphenyls and α, α' -binaphthyl would be understandable if the absorption curve of the α, α' -binaphthyl extended to longer wavelengths than those of the terphenyls. Therefore, by means of a monochromator and photomultiplier arrangement, a more complete check of the absorption curves of *m*-terphenyl and α, α' -binaphthyl was made in a range where pertinent data were not previously available. (*M*-terphenyl was chosen because of its greater solubility.) The concentrations were chosen in such a way that both the *m*-terphenyl and the α, α' -binaphthyl solutions had practically equal absorption at shorter wavelengths where a maximum in the absorption curve occurs. Then the relative absorption was observed at a series of longer wavelengths. These experiments showed that the absorption spectrum of α, α' -binaphthyl extends to slightly longer wavelengths than that of *m*-terphenyl, which in turn shows that the lowest excitation energy of *m*-terphenyl is greater than that of α, α' -binaphthyl. This supports our explanation that energy transfer to terphenyl from naphthalene does not occur because the excitation energy of terphenyl is too high. The occurrence of the small fluorescence of *m*-terphenyl in the solvent combination

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¹ H. Kallman and M. Furst, *Phys. Rev.* **79**, 857 (1950).

² M. Furst and H. Kallman, *Phys. Rev.* **94**, 503 (1954).

³ A more complete discussion of this system will be given in a paper now in preparation.

⁴ R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds* (John Wiley and Sons, Inc., New York, 1951).

shows that the energy level of terphenyl may nevertheless be slightly above that of naphthalene.

From these experiments, two conclusions may be drawn. First, a sharp drop in energy transfer only occurs when the excitation energy of the solute molecule is very close to (or below) that of the transferring molecule. α, α' -binaphthyl and naphthalene have lowest energy levels which are fairly close to each other; however, despite this small energy difference the energy transfer is just as efficient as to other solute molecules which have much lower energy levels, e.g., 2, 5-diphenyloxazole. If the energy level of the molecule is below the energy level of the solvent molecule (or perhaps extremely close), the energy transfer ceases to occur. Second, these experiments show that the lowest (singlet) state of the naphthalene molecule is responsible for the energy transfer; otherwise the terphenyls would be excited by the excited naphthalene molecule. It is known both from theoretical considerations and from absorption curves that the lowest singlet state of naphthalene has only a very small transition probability to its ground state.⁵ The dipole moment associated with this transition in naphthalene is about 100 times smaller than that for many other molecules of this type. In spite of this low dipole moment, the energy transfer from naphthalene to various solute molecules is almost as efficient as that from molecules which have larger dipole moments associated with the transitions from their lowest excited singlet states. If one now assumes that the true lifetime of these excited solvent molecules

is not determined by their transition dipole moment (since these molecules in large concentration display only very little emission), then these results may be taken as an indication that the energy transfer between excited molecules in these liquid systems is not so much caused by a dipole interaction but rather by an interaction over small distances when the excited and accepting molecules are very close to each other as in a collision.

These results together with experiments previously performed show that high-energy-induced fluorescence in dilute solutions, and thus energy transfer from the solvent to the solute, occurs strongly only when the lowest excitation energy (of the singlet state) of the solvent molecule is greater than that of the solute. Even in such cases, however, it does not necessarily occur since the transfer also depends upon the lifetime of the excited solvent molecule. These results (that such transfer drops sharply when the excitation energies come close to each other, and that it is always very small, if it occurs at all, when the solute excitation energy is smaller than that of the solvent) are in agreement with our theory¹ that the energy transfer comes about by a transfer of the lowest excitation energy. These experiments again show² that a theory based on energy transfer by means of short-wave radiation⁶ is not suitable to account for the observed phenomena.

⁵ M. Kasha and R. V. Nauman, J. Chem. Phys. **17**, 516 (1949).

⁶ J. B. Birks, *Scintillation Counters* (Pergamon Press, London; McGraw Hill Book Company Inc., New York, 1953); Phys. Rev. **94**, 1567 (1954); **95**, 277 (1954).