

studies show the transition moment to lie along the C-I bond.

NH(A $^3\Pi$) and OH(A $^2\Sigma^+$) substitutional guests have localized rotational motions. Temperature dependent NH A \rightarrow X emission spectra are analyzed to show that NH(A $^3\Pi$) librates, with a several hundred cm^{-1} barrier to free rotation, while the ground X $^3\Sigma^-$ state almost freely rotates. Both NH (A $^3\Pi$) and OH(A $^2\Sigma^+$) strongly violate a proposed vibrational relaxation energy gap law, in that hydride rates are faster than deuteride rates. This violation, coupled with the absence of typical multiphonon temperature dependence, appears to reflect use of the rotational local mode as the phonon accepting mode. However, intersystem crossing by NH(A $^3\Pi$, $v' = 0$) shows the strong temperature dependence characteristic of stimulated phonon emission, and delocalized lattice phonon modes appear to accept energy in this case.

H4

Chemiluminescence from the Degradation of Unsaturated Elastomers

G. D. MENDENHALL and R. A. NATHAN
Battelle-Columbus Laboratories, Columbus, Ohio 43201 (U.S.A.) and

M. A. GOLUB
Ames Research Center, NASA, Moffett Field, Calif. 94035 (U.S.A.)

The autoxidation of thin films of *cis*-1,4-polyisoprene in oxygen in the temperature range 25 - 126°C was studied by the weak chemiluminescence emission accompanying the process. The mechanism was assumed to involve a conventional free-radical oxidation chain with electronic excitation in the termination steps. From the time and temperature dependence of the intensity of the emission, activation parameters were obtained for some of the reaction steps. Chemiluminescence emission was also studied from a sample of *cis*-1,4-polyisoprene containing hydroperoxide groups that were introduced by means of singlet molecular oxygen.

An apparatus for measurement of the chemiluminescence was described.

This research was supported by Contract NAS2-8195 of the National Aeronautics and Space Administration.

J2

The Thermodynamics of Photochemical Energy Conversion, and Its Relevance to Photochemical Solar Energy Conversion

M. D. ARCHER

The Royal Institution, 21 Albemarle Street, London W1X 4BS (U.K.)

This paper is addressed to the following questions: what is the maximum efficiency with which radiant energy may be turned into other forms of energy, and in particular into electrical energy (as in a photoelectric device) or into chemical free energy (as in an endergonic photochemical reaction)? Are such energy converters subject to thermodynamic restraints of the type that limit the performance of heat engines, or are they capable, at least in principle, of perfectly efficient conversion? What are the implications of any theoretical limitations on maximum efficiency for solar energy conversion?

These questions have been posed and answered in a number of ways in the literature already. Although disagreement with the application of thermodynamic arguments to photon absorption processes has occasionally been expressed [1, 2], it has generally been concluded [3 - 12] that the maximum efficiency of a radiant energy transducer is given by an expression of the type

$$\eta \leq 1 - T_s/T_L \quad (1)$$

Here T_s is the temperature of the absorbing system and T_L is the temperature of the incident light — a concept that is unfamiliar to the majority of physical chemists. It is defined in most general form by the relationship

$$T_L = \dot{E}_L/\dot{S}_L \quad (2)$$

where \dot{E}_L and \dot{S}_L are the rates at which the incident light adds energy and entropy to the absorbing system. In particular cases (e.g. for black body radiation) T_L may be more explicitly defined, and numerical estimates of η may be made.

In energy converters which produce light from work (e.g. from electrical work, as in a light-emitting diode), analogous reasoning [13 - 16] leads to an expression for the maximum efficiency of conversion of work to radiant energy of the type:

$$\eta < (1 - T_s/T_L)^{-1} \quad (3)$$

Such a device can therefore, in principle, act to a slight extent as a refrigerator, as it is able to convert all of the inflowing work and a fraction T_s/T_L of the heat flowing to it from its surroundings into "high grade" radiant energy [17].

This review paper will present a unified treatment of the published work on these subjects, outline the reasoning that leads to the above conclusions, and explain the implications for direct solar conversion and for photochemical processes generally.

- 1 D. Kahn, *Plant Physiol.*, 36 (1961) 539.
- 2 P. Suppan, Paper E114, UNESCO Conference, "The Sun in the Service of Mankind", Paris 1973, Centre Nationale d'Etudes Spatiales, B.P. No. 4, 91220 Bretigny-sur-Orge, France.
- 3 L. N. M. Duysens, in "The Photochemical Apparatus: Its Structure and Function", Brookhaven Symposia in Biology, No. 11, 1958, pp. 18-20.
- 4 W. Brittin and G. Gamow, *Proc. Nat. Acad. Sci. U.S.A.*, 47 (1961) 724.
- 5 R. G. Mortimer and R. M. Mazo, *J. Chem. Phys.*, 35 (1961) 1013.
- 6 W. Shockley and H. J. Queisser, *J. Appl. Phys.*, 32 (1961) 510.
- 7 A. Rose, *J. Appl. Phys.*, 31 (1960) 1640.
- 8 R. T. Ross, *J. Chem. Phys.*, 45 (1960) 1.
- 9 R. T. Ross, *J. Chem. Phys.*, 46 (1967) 4590.
- 10 R. T. Ross and M. Calvin, *Biophys. J.*, 7 (1967) 595.
- 11 W. Yourgrau and A. van der Merwe, *Proc. Nat. Acad. Sci. U.S.A.*, 59 (1968) 734.
- 12 R. S. Knox, *Biophys. J.*, 9 (1969) 1351.
- 13 G. C. Dousmanis, C. W. Mueller, H. Nelson and K. G. Petzinger, *Phys. Rev.*, 133 (1964) A316.
- 14 P. T. Landsberg and D. A. Evans, "Proceedings of the International Conference on Luminescence", Budapest 1966, Hungarian Acad. Sci., pp. 1882-1890.
- 15 P. T. Landsberg and D. A. Evans, *Phys. Rev.*, 166 (1968) 242.
- 16 W. Feist and G. Wade, *J. Appl. Phys.*, 41 (1970) 1799.
- 17 M. A. Weinstein, *J. Opt. Sci. Am.*, 50 (1960) 597.

K1

Product Vibrational Distribution from Photo-Induced Dissociation Processes

K. F. FREED and Y. B. BAND

The James Franck Institute and The Department of Chemistry, The University of Chicago, Chicago, Ill. 60637 (U.S.A.)

Luminescence measurements have been used to determine the vibrational dissociation processes of isolated molecules in cases where the products are formed in excited electronic states. Experimental data currently exist for RCN photodissociation to produce CN in the $B^2\Sigma^+$ and $A^2\Pi$ states ($R = H, I, CN, CH_3, \dots$) and for CO_2 photodissociation to triplet states of CO. West and Berry have shown in the former case how this phenomenon can be used to generate photodissociation lasers from both electronic and vibrational population inversions.

Previous theories of photodissociation in polyatomic molecules are based upon a quasi-diatom model which ignores the often drastic change of the normal modes in the transition from the initial state to the photofragments. Likewise the quasi-diatom models are deficient in assuming that the reaction coordinate for the dissociation is also a normal coordinate in the initial molecular electronic state.

Our model considers the case of the collinear photodissociation of polyatomic molecules and employs the correct (and different) normal modes for the initial state and the photofragments. The full multi-dimensional bound-continuum Franck-Condon factors are exactly reduced to one-dimensional bound-continuum integrals for which an analytical approximation can readily be made. During the recoil of the photofragments, the "half-collision", forces between the fragments can result in changes in the purely Franck-Condon vibrational distribution. This vibrational relaxation is treated using a simple semi-classical model, but any of the more detailed standard methods of collision theory can readily be employed for the half-collision.

Calculations to date involve the HCN and ICN systems (work on CO_2 is in progress) where good agreement with