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

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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.

J2
The Thermodynamics of Photochemical Energy Conversion, and Its Relevance to Photochemical Solar Energy Conversion

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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 phtochemical 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

$$\eta \leqslant 1 - T_s/T_L \qquad (1)$$

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

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

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:

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