

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.

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Product Vibrational Distribution from Photo-Induced Dissociation Processes

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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

experiment is readily obtainable through minor adjustments in the diatomic-like repulsive potential between the fragments. More interesting is the fact that the theory provides simple explicit criteria for the occurrence of fragment vibrational population inversions solely on the basis of known spectroscopic constants for the molecule and for the fragments and of the diatomic-like repulsive potential.

Model calculations indicate the possibility of generating large isotope effects in photodissociation processes by a suitable tailoring of the molecule. The absolute isotope effect is predicted to depend exponentially on the square root of the isotopic ratios of the reduced mass of the departing atom with respect to the remaining molecular fragment.

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(Invited Lecture)

Infrared Laser Enhanced Reaction Dynamics

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To date considerable kinetic information has been derived on state selected chemical reactions [1, 2] by Polanyi and co-workers employing the "arrested relaxation infrared chemiluminescence method" which probes vibrational and rotational energy distributions in reaction products formed in fast reactions (*e.g.* reactions of the exchange type $A + BC \rightarrow AB + C$). Information about the details of the potential surfaces characterizing reaction systems can in principle be obtained through trajectory computations.

Now that infrared lasers are available, which are either continuously tunable, or which emit discrete emissions that can be matched to specific infrared molecular absorptions employing a magnetic or electric field, the unique possibility of producing high concentrations of diatomic and multi-atomic reactants in specific vibrational states and measuring the specific

effect of vibrational energy on reaction kinetics becomes possible. A brief description of the methodology will be presented *i.e.* available laser systems and techniques for performing infrared "laser enhanced reaction dynamics" measurements. Either real-time kinetic measurements, or depth of modulation measurements can be made; the former is suitable to measuring reactions rapid compared to vibrational relaxation times, the latter must be employed if reaction rates are very slow compared to vibrational relaxation times. From these types of experiments two kinds of information can be obtained. The specific effect of vibrational energy on increasing (or possibly decreasing) the absolute reaction rate can be determined [3]. Can these state selected reactions be described by an Arrhenius formulation and if so does the energy of activation or the pre-exponential (or both) change if vibrational energy is added to one of the reactants? [4]. Several phenomenological formulations will be discussed and compared with recent data. A second kind of information that can be derived is similar to that obtained from the "arrested relaxation infrared chemiluminescence method". The distribution of energy in product molecules can be probed either by measuring the visible or u.v. emission from specific chemiluminescence reactions [5, 6] or product molecules can be probed during various stages of relaxation by using continuously tunable dye lasers. The effect of reactant vibrational energy on the distribution of energy in reaction products is clearly discernible and the results of several chemiluminescent reaction systems will be discussed. Implications of present results on theory of chemical reactions will be presented and suggestions for future experiments will be briefly outlined.

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