

Figure 2. Reflection spectra of anthracene crystal before (1) and after (2) photo-oxidation.

### T6

#### Vibrational Relaxation in Condensed Media

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A master equation approach has been developed to describe the vibrational relaxation and a model for calculating the rate constant of vibrational relaxation in condensed media based on the assumption that the short-range repulsive portion of the intermolecular force is responsible for inducing the vibrational relaxation has been presented [1, 2].

In this investigation, we are concerned with the temperature effect on vibrational relaxation and the vibrational energy transfer from the vibrationally excited donor to the acceptor. For the temper-

ature effect, we present numerical results to show the temperature dependence of the rate constant of vibrational relaxation and to discuss the validity of the rate constants obtained from the use of the weak coupling approximation and the strong coupling approximation. It is shown that although the temperature effect is extremely large over the temperature range  $T = 0$  to  $T = \theta_E$ , the Einstein temperature of the medium, for the temperature range  $T = 0$  to  $T = 0.3 \theta_E$ , the rate constant varies slowly with temperature.

For the vibrational energy transfer, we derive the master equation to describe the time dependent behavior of the excited donor, and the expression for the rate constant of vibrational energy transfer. The master equation is solved to study the temporal behavior of the excited donor as a function of the acceptor concentration. Numerical results are presented to demonstrate the theoretical results.

- 1 G. R. Fleming, O. L. J. Gijzeman and S. H. Lin, *J. Chem. Soc., Faraday Trans. II*, 70 (1974) 37.
- 2 S. H. Lin, *J. Chem. Phys.*, 61 (1974) 3810.

### T8

#### $C_2^-$ Molecular Ion: Long Range Electron Tunnelling and $B^2\Sigma_u^+ \leftrightarrow a^4\Sigma_u^-$ Intersystem Crossing in Rare Gas Lattices

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The  $B^2\Sigma_u^+$  fluorescence of  $C_2^-$  displays an extreme Personov effect — narrowing in emission of an inhomogeneously broadened absorption spectra excited by monochromatic light. The temperature dependent single site emission spectra are consistent with Rebane impurity spectra theory and quadratic electron-phonon coupling.  $C_2^-$  appears to be a substitutional guest in Ar, Kr, and Xe, and to displace two or more atoms in Ne. The principal vibrational relaxation pathway within the B state involves sequential steps through two vibrational levels of the previously predicted (yet unobserved)

a  $^4\Sigma_u^-$  state, whose origin lies about  $1100\text{ cm}^{-1}$  above the B state. Both the vibrational relaxation rate (strongly temperature and isotopic mass dependent) and  $v' = 0$  lifetime of a  $^4\Sigma_u^-$  are monitored in this manner. A superficially random variation of B state lifetimes among  $^{12}\text{C}^{12}\text{C}^-$ ,  $^{12}\text{C}^{13}\text{C}^-$ , and  $^{13}\text{C}^{13}\text{C}^-$  reflects accidental coincidences with high levels of the  $\text{A}^2\Pi$  state. The purely radiative lifetimes are near 65 ns in Ne, 40 ns in Ar, 38 ns in Kr, and 34 ns in Xe.

The formation of "stable" ions in  $1216\text{ \AA}$  photolyzed, acetylene doped rare gas lattices is shown to be consistent with single photon ionization schemes using dielectric physics ideas. A long range electron tunnelling from the excited B state of  $\text{C}_2^-$  in Ne to a nearby (*ca* 10 - 15 Å) cation is observed. The rate is  $K_1 \approx 10^3\text{ s}^{-1}$  and increases with vibrational level.

Fluorescence and radiationless transitions in  $\text{Br}_2$  and  $\text{Cl}_2$  have also been studied. In  $\text{Br}_2$ , the emitting state is identified by its excitation spectrum as the  $\text{B } ^3\Pi(\text{O}_u^+)$ , and the lifetimes in different matrices suggest a gas phase  $v = 0$  radiative lifetime of  $11 \pm 1\text{ }\mu\text{sec}$ . In  $\text{Cl}_2$ , the emission following either  $\text{B } ^3\Pi(\text{O}_u^+)$  or  $^1\Pi_1$  excitation occurs from a long-lived ( $\sim 100\text{ ms}$ ) electronic state lying  $620\text{ cm}^{-1}$  below the B state. We tentatively assign this state as  $^3\Pi_2$ .

## V1 (Invited Lecture)

### Chlorocarbon Compounds and Stratospheric Ozone

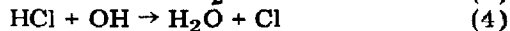
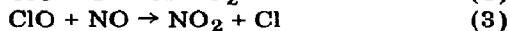
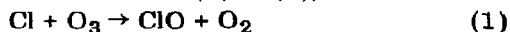
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Two chlorofluoromethane compounds,  $\text{CF}_2\text{Cl}_2$  and  $\text{CFCl}_3$ , are widely used in current technology as aerosol propellants, refrigerants, solvents and in the blowing of polyurethane foam. These uses led in 1974 to the release to the atmosphere of approximately  $5 \times 10^5$  and  $3 \times 10^5$  tons, respectively, of these gases. Since the molecules are normally inert chemically, biologically unreactive, insoluble in water and transparent and visually near u.v. radiation, they have long environmental lifetimes and are accumulating in the earth's atmosphere.

The present levels are in the vicinity of 1 part in  $10^{10}$  by volume for each.

Both molecules are decomposed by ultraviolet light with  $\lambda$  less than about  $2200\text{ \AA}$ , releasing one Cl atom; the subsequent reaction of the residual radical with  $\text{O}_2$  releases another chlorine entity (either ClO or Cl). Since such hard u.v. radiation is absorbed well by both  $\text{O}_2$  and  $\text{O}_3$  in the atmosphere, the chlorofluoromethanes must rise into mid-stratosphere ( $> 20\text{ km}$ ) before any appreciable photodecomposition occurs in the atmosphere. The chlorine atoms released between 20 - 35 km initiate a chain reaction with  $\text{O}_3$  in which the most important reactions are (1) to (5),



and for which the chain-length before eventual termination is  $> 10^4$ . Detailed calculations indicate a present average depletion of the ozone layer approaching 1%, and future steady-state depletions of 10% or more for continued release of  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCl}_3$ , and other halocarbons at the 1973 rates. Depletion of the  $\text{O}_3$  layer has many possible biological and climatic consequences.

The slow upward diffusion of molecules in the stratosphere ensures a delay between ground-level release and the full effect on the ozone layer — the maximum depletion for molecules released in 1974 will occur in 1985 - 1990. In addition, the estimated atmospheric lifetimes for these molecules are so long (40 - 150 years) that approximately a century will be required for the ozone depletion to decrease to one-half its maximum value.

Other halocarbon compounds are also present in the atmosphere, some of natural (*e.g.*  $\text{CH}_3\text{Cl}$ ) and many of anthropogenic origin. In general, molecules containing C - H bonds or C = C bonds have much less stratospheric hazard per molecule because they are largely removed by tropospheric reactions with OH radicals. Molecules such as  $\text{CCl}_4$ ,  $\text{CCl}_3\text{F}_3$ , etc., also are expected to react predominantly in the stratosphere.

Current estimates indicate that the average ozone level of the stratosphere will