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THE DYNAMICS OF VIBRATIONALLY EXCITED MOLECULES(U)
CALIFORNIA UNIV BERKELEY DEPT OF CHEMISTRY C B MOORE
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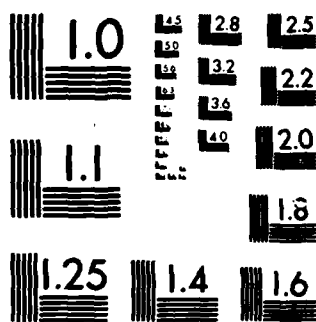
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20. ABSTRACT The purpose of this work has been to study the transfer of vibrational energy among molecular degrees of freedom and the chemical reactions of vibrationally excited molecules. By resolving the dependence of energy transfer and reaction processes on quantum numbers the mechanism of and forces involved in these processes are identified.		

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FINAL REPORT

PROPOSAL NUMBER: DRXRO-PR P-18039-CH

PERIOD COVERED BY REPORT: May 25, 1981 - December 31, 1984

TITLE OF PROPOSAL: The Dynamics of Vibrationally Excited Molecules

CONTRACT OR GRANT NUMBER: DAAG29-81-K-0079

NAME OF INSTITUTION: Department of Chemistry
University of California
Berkeley, CA 94720

PRINCIPAL INVESTIGATOR: Professor C. Bradley Moore

I. Statement of Problem:

The purpose of this work has been to study the transfer of vibrational energy among molecular degrees of freedom and the chemical reactions of vibrationally excited molecules. By resolving the dependence of energy transfer and reaction processes on quantum numbers the mechanism of and forces involved in these processes are identified.

II. Principal Results:

1. Vibrational relaxation of molecules trapped in rare gas matrices.

Experiments on HCl (14), CH₃F (4) and HCN (15,16,19) have revealed that vibrational energy transfer in solid matrices is usually analogous to vibrational energy transfer in gas phase binary collisions. For CH₃F and HCN relaxation occurs in hard collisions with the repulsive cage walls. The rates depend linearly on vibrational quantum number as expected for harmonic oscillators in first order. Energy transfers among vibrational modes ($V \rightarrow V$) are usually fast compared to coupling to the lattice. Vibrational energy is usually removed from a polyatomic stepwise through its lowest energy vibrational degree of freedom. Detailed intramolecular $V \rightarrow V$

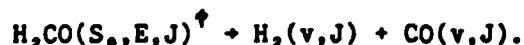
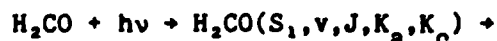
studies in HCN, DCN and HC^{13}N in Xe reveal for the first time that gas phase rules work for the dependence of rates on quantum number changes and energy discrepancy transferred to the lattice. For HCN an anomaly occurs which causes the CN stretch to relax less rapidly than the bend; the resulting population inversion could be used for laser action just as in the gas-phase CO_2 laser. A first quantitative test of resonant intermolecular $V \rightarrow V$ transfer by dipole-dipole interaction demonstrated the quantitative usefulness of the Förster theory. For HCl (14) relaxation is shown to occur as a result of attractive interactions in much the way that rapid energy transfer is seen in gas phase for strongly hydrogen bonded systems (7).

2. High overtone spectroscopy and photochemistry.

The high overtone spectra ($v = 4, 5, 6$) of CH stretches exhibit peaks assignable to single local mode bond stretches (1,3,5). This excitation can be sufficient to cause chemical reaction (12). We have found (8) for 2-methyl cyclopentadiene that the rate of 1-5 hydrogen shift is independent of which C-H bond is excited by the visible laser. Excitation of the C-H bond to be broken was no more effective than excitation of one remote from the site of reaction. Energy transfer is much faster than isomerization in this molecule. A laser pyrolysis method of measuring unimolecular reaction barriers was developed (6) to obtain accurate data for vibrational photochemistry experiments. The quantum yield for $\text{H}_2\text{O} + h\nu \rightarrow \text{H}^+ + \text{OH}^-$ in liquid water was found to increase strongly with vibrational quantum number (2). The quantum yields are in the 10^{-4} to 10^{-9} range; thus chemical reaction competes, though rather poorly, with energy transfer. Vibrational relaxation in liquid water must occur on a sub-picosecond timescale. Studies of this relaxation in gas phase were extended to D_2O , D_2S and H_2Se (7).

3. Photofragment spectroscopy.

The formaldehyde molecule has been excited to single rovibronic levels of its first excited singlet state and the quantum states of dissociation products fully resolved.



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The nuclear spin quantum number of the hydrogen was proven to be conserved (odd $K_a \rightarrow$ odd J_{H_2}) in the dissociation. The excited electronic state internally converts to the ground state; dissociation occurs by crossing over and tunneling through a high barrier on the ground state potential surface (11). Strong repulsion in the exit valley gives strong rotational excitation of CO (17). H_2 is found to be significantly vibrationally and rotationally excited (20). Quantum-state-by-quantum-state comparison of results to fully ab initio theory is possible. Excellent qualitative agreement with dynamics expected from the ab initio transition state structure is obtained. The H_2 pushes away from the CO with a force pointed at the electron distribution beyond the C nucleus. Photofragments separate rapidly compared to the rate for energy transfer among degrees of freedom.

The CO v, J distribution produced by uv excitation of ketene $CH_2CO + 308 \text{ nm} \rightarrow CH_2 + CO(v, J)$ is found to be statistical (18). Dissociation occurs over a threshold rather than a barrier and energy transfer among degrees of freedom occurs rapidly on the timescale of photofragment separation.

III. Publications:

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