Progress Report

Contract No. E(11-1)- 3498

Fundamental Studies in Isotope Chemistry

between

Division of Research

U.S. Energy Research and Development Administration

and

University of Rochester

MASTER

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Abstract

During the past year we have confirmed the coupling between the translational and rotational potential energy in solid and liquid CO_2 by measurements on the similar molecule N_2O. Vapor pressures of $^{15}N^{14}N^{16}O$, $^{14}N^{15}N^{16}O$, and $^{14}N^{14}N^{18}O$ have been measured over the range 143 - 182° in the solid and 182 - 219° in the liquid. The liquid data fulfill the requirement that the shift in the internal vibrational energies from the gas to condensed phase vanishes at the critical temperature. The temperature dependence of the internal zero point energy shift leads to a pseudo temperature independent term in the logarithm of the vapor pressure ratio. The results of these linear molecules form the basis for the calculation of the vapor pressures of all the isotopic species of OCS. ^{18}OCS is predicted to have a large translational-rotational coupling.

The first measurements of the isotopic fractionation factors for two components in a solution have been made as a function of concentration in argon-krypton mixtures. The measurements cover the range from pure argon to pure krypton and extrapolate very well to our previous measurements on the pure components. The mean square force on Kr in an infinitely dilute solution of Ar has been found equal to the mean square force on Ar in an infinitely dilute solution

in krypton. The latter result suggests that three body forces
make a small contribution to $\langle \nabla^2 U \rangle$. A calculation of $\langle \nabla^2 U_{ij} \rangle$
(i = argon, j = krypton) as a function of the mole fraction
of krypton by the WCA perturbation method is about 25% larger
than the experimental value for mole fractions of krypton $> \frac{1}{2}$.
The discripancy is most probably associated with the theory
of mixtures rather than the potential parameters.

Last year we published jointly with Ishida a major
analysis of the isotope chemistry of hydrogen and deuterium
in a number of important reference molecules, e.g., H_2O,
HC_4, C_2H_6, C_2H_4, CH_2O, and C_6H_6. The principal results were:
(1) stretching vibrations account for about 70% of the dif-
ference in isotope chemistry at room temperature and become
an even larger fraction of the isotope chemistry at higher
temperatures. This result has been analyzed in terms of the
ratio of stretching and bending force constants and the
statistical mechanics of an oscillator as a function of the
magnitude of $h\nu/kT$, the vibrational energy as a function of
temperature. It is found that there is remarkable additivity
in the isotope chemistry of hydrogen and deuterium even at
room temperature. This result has been explained in terms
of the structures of molecules containing hydrogen atoms.
The hydrogen atom can form only one single bond except for
the unique case of hydrogen bonding. It is therefore always

a terminal atom and the vibrations of the molecule contain
little coupling of bending and stretching motions.

The results evoked wide interest from a wide audience
of chemists. The method has now been extended to the iso-
tope chemistry of carbon and oxygen. The general features
found in the isotope chemistry of hydrogen are repeated
for carbon and oxygen with one major exception. Heavy
atom isotope effects at room temperature are not strictly
additive. The deviations from additivity can be traced
directly to the coupling between stretching and bending
modes which exists for non-linear Y-X-Z groupings.

A new class of sum rules related to the $\underline{H}^j(\underline{GF})^j$, matrices
which describe the molecular vibrations of polyatomic mole-
cules have been derived in a joint research with Ishida.
It is shown that subrules local to sets of euqivalent co-
ordinates exist in addition to the sum rules formed over
the common symmetry classes or the totality of molecular
eigenvalues. The rules are conveniently expressed in matrix
form, $\underline{D}$, related to the $\underline{H}$ matrices of order j for a series
of isotopic homologues. The first and second order $\underline{D}$

matrices for all important structural types have been derived
and used to analyze the deviations from the first rule of
the mean. The $\underline{D}$ matrix formulation provides a very good
physical insight into the origin of deviations from the

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rule of the mean. Even at the level of $\underset{\sim}{D}^2$, the $\underset{\sim}{D}$ matrix formulation, combined with the finite orthogonal polynomial method, gives an excellent approximation to the exact values for isotopic disproportion reactions in molecules such as water and methane at room temperature and within the HOBO approximation.

Publications

Y. Yato, M. W. Lee, and J. Bigeleisen. Phase Equilibrium
Isotope Effects in Molecular Solids and Liquids.
Vapor Pressures of the Isotopic Nitrous Oxide
Molecules. J. Chem. Phys. 63, 1555 (1975).

J. Bigeleisen, et alia., The Proposed National Resource
for Computation in Chemistry: A User-Oriented Facility.
National Research Council - National Academy of
Sciences, Washington, D.C., June 1975.

J. Bigeleisen, R. C. Hom, and T. Ishida. Isotope Chemistry
and Molecular Structure. Carbon and Oxygen Isotope
Chemistry. J. Chem. Phys. 64, 3303 (1976).

T. Ishida and J. Bigeleisen. Isotope Chemistry and Molecular
Structure. Deviations from the First Rule of the Mean.
J. Chem. Phys. 64, 4775 (1976).

Reports Issued

COO-3498-24 Progress Report

COO-3498-26 Isotope Chemistry and Molecular Structure.
Deviations from the First Rule of the Mean.
T. Ishida and J. Bigeleisen. J. Chem. Phys. 64,
4775 (1976).

COO-3498-27 Closed System Gas Circulating Pump, F. J. Torre,
D. M. Eshelman, M. W. Lee, P. Neufeld, and
W. Watson, Review of Scientific Instruments,
to be published.

Reports (continued)

COO-3498-28 Isotope Chemistry and Molecular Structure.

Carbon and Oxygen Isotope Chemistry.

J. Bigeleisen, R. C. Hom, and T. Ishida,

J. Chem. Phys. $\underline{64}$, 3303 (1976).

Lectures and Talks

1. "Mean Square Force in Simple Liquids and Solids",
   Ben-Gurion University - Beer Sheva, Israel, 10 June 1975.

2. "Dependence of the International Energy Pool on Isotope
   Separation Processes", Ben-Gurion University - Beer Sheva,
   Israel, 17 June 1975.

3. "Dependence of the International Energy Pool on Isotope
   Separation Processes", Weizmann Institute for Science,
   Rehovot, Israel, 20 June 1975.

4. "Relationship of Molecular Structure to Isotope Chemistry",
   Technion - Haifa, Israel, 23 June 1975.

5. "Translation - Rotation Coupling in Molecular Solids and Liquids",
   25th IUPAC Congress, Jerusalem, Israel, 7 July 1975.

6. "Planning the National Resource for Computation in Chemistry:
   Organization and Administrative Structure to Serve the
   User Community", American Chemical Society Meeting,
   Chicago, Illinois, 27 August 1975.

7. "National Resource for Computation in Chemistry", American
   Institute of Chemical Engineers, Los Angeles, 27 August 1975.

8. "Isotope Chemistry and Molecular Structure", University of
   Tennessee, Knoxville, 9 March 1976.

Professional Activities

Visiting Committee, Carnegie-Mellon University.

Visiting Committee, AUA, Argonne National Laboratory.

Consultant, Oak Ridge Gaseous Diffusion Plant.

Consultant, Los Alamos Scientific Laboratory.

Visiting Scientist, Weizmann Institute.

John Simon Guggenheim Fellow.

Nation Research Council – National Academy of Sciences

    a. Committee to Plan the National Resource in

        Computational Chemistry (Chairman).

    b. Assembly of Mathematical and Physical Sciences,

        (Chairman).

Scope of Activities

The principal investigator is Professor of Chemistry and
Tracy H. Harris Professor of Mathematics and Natural Philosophy
in the College of Arts and Science at the University of
Rochester, where is active in undergraduate teaching,
graduate instruction, research, and university affairs.
During the past year he has continued as a consultant to the
isotope separation programs at Oak Ridge and Los Alamos.
He has been invited to extend his consulting activities to
include Lawrence Livermore Laboratory.

The principal investigator is, by arrangement with the
University of Rochester, a part time officer of the National
Academy of Sciences - National Research Council. He is
Chairman of the Assembly of Mathematical and Physical
Sciences with policy and operating responsibilities in all
areas of the mathematical and physical sciences, including
chemistry, physics, mathematics, earth sciences, geophysics,
space science, statistics, and international programs in
these areas. He is currently Chairman of the Committee for
Planning the National Resource for Computation in Chemistry.