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A PHOTOIONIZATION STUDY OF CLUSTER SPECIES PRESENT IN GAS VAPORS

AND THOSE CREATED BY CONDENSATION IN

A SUPERSONIC MOLECULAR BEAM

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18. SUPPLEMENTARY NOTES

Part of the material described herein has been submitted for publication. Much has been discussed at various national and international conferences.

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

Photoionization, molecular beam, condensation, nucleation, synchrotron radiation

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

This interim report summarizes the results of studies on clusters sampled by and produced through a supersonic molecular beam sampling system. Photoionization cross section measurements were used to calibrate mass spectral ion signals and to study beam discrimination effects. Heats of formation data were obtained for clusters of carbon dioxide, methanol, methanol-d_1, ethanol, and trifluoroethanol.

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I. SUMMARY

This report summarizes the accomplishments made in the second year grant period toward the objectives of the proposed work on cluster species produced in a supersonic molecular beam. The effort has been productive in understanding the energetics of carbon dioxide clustering as a consequence of the beam expansion. Evidence has also been accumulated to quantify analytical sampling of gases in the sample source before expansion. Critical experiments are described which attempt the evaluation of the equilibria of the methanol clusters which are originally present in the nozzle before expansion. Results of the research have been published and progress accounts have been presented at several national and international conferences.

II. INTRODUCTION

Supersonic molecular beams can be operated to produce cluster species whose energetics of formation can be important to the understanding of nucleation and cluster growth phenomena. The beams can also be used for sampling purposes whereby a gas mixture at relatively high pressure can be transported into a region of much lower pressure. At the reduced pressure a variety of analytical techniques can be employed to probe the composition of the sample gas. If the sampling technique is mass spectrometry, the quantitative relationship must be established among species concentrations, ion signals measured by the mass spectrometer, and the conditions (pressure, temperature, gas composition, nozzle-skimmer distance, etc.) which define the operation of the supersonic molecular beam. The research over this report period has been directed toward providing some of those quantitative relationships, and has the following objectives:

a. To utilize photoionization to provide the mass spectrometer signals so that both the energy and bandwidth of the excitation can be limited by the monochromator settings. (Our continuous vacuum ultraviolet light source is provided by dispersed synchrotron radiation.)

b. To predict the expected mass spectrometer ion signals from measured absolute photoionization cross sections and to utilize the differences between predicted and observed ion signals to calibrate the mass spectrometer response. Coupled with this is the attempt to describe quantitatively the mass discrimination which occurs as a beam is produced from a mixture of light and heavy molecular weight gases.

c. To study in detail two types of molecules which appear to show different cluster and/or nucleation behavior depending on beam conditions. These systems are the hydrogen bonded clusters represented by alcohols and van der Waals type clusters, such as carbon dioxide.

We chose to use photon ionization because the energy resolution can be quite high (on the order of 0.005 eV). Both the energy input and resolution are controlled by the photon monochromator parameters. Synchrotron radiation produced from a storage ring was chosen as the photon source because it produced a true continuum of high intensity and stability over the wavelength range of interest. Photoionization measurements offered the possibility that absolute ionization cross section measurements could be used to calibrate the mass spectrometer ion intensities, and the wavelength for cluster examination could be chosen such that fragmentation of larger clusters to form smaller clusters could be prevented from obscuring the desired cluster intensity information. Alcohols were chosen as examples of hydrogen bonded interaction because alcohol clusters were found to be formed before the expansion of the supersonic molecular beam. Carbon dioxide was chosen as an example of the non-hydrogen bonding interaction. Clusters of CO_2 are formed as a consequence of the beam expansion process.

III. BRIEF SUMMARY OF RESULTS

Work under the Navy contract began on May 1, 1975 and the following summarized results have been obtained to date.

A. van der Waals Clusters of Carbon Dioxide. The cluster reactions of carbon dioxide have been investigated and a tentative heat of formation of the dimer has been obtained. The clusters formed as a consequence of the beam expansion and conditions can be obtained to produce the dimer to the exclusion of higher polymers as well as to produce large molecular weight polymers. A major paper by G. G. Jones and J. W. Taylor describing the results of this study entitled, "A Photoionization Study of Carbon Dioxide Dimers in a Supersonic Molecular Beam", is in press to J. Chem. Phys. The abstract follows:

Photoionization of carbon dioxide clusters from a supersonic molecular beam using wavelength dispersed synchrotron VUV radiation revealed that neutral cluster formation was dominated by growth in the molecular beam expansion jet. The photoionization efficiency curve of the carbon dioxide dimer at m/z 88 differed from the monomer curve at m/z 44 in that the onset was strongly curved and shifted 0.37 eV lower than the sharp m/z 44 onset at 13.77 eV. The few remaining autoionization features from the dimer ion were strongly broadened. Three broad autoionization features in the m/z 88 curve were fit to a Rydberg series with a convergence limit of 18.04 eV. This series had peaks and quantum defects close to that for the Henning diffuse series which converges to the $B ^2\Sigma_u^+$ electronic state of the CO_2^+ ion at 18.076 eV. The slight shift to lower energy of the m/z 88 series limit was tentatively related to the neutral dimer bond energy. Through the use of a thermodynamic cycle and the observed m/z 88 ionization onset, the lower limit to the exothermicity of the reaction of CO_2^+ with CO_2 to form $(CO_2)_2^+$ was predicted to be 7.2 kcal/mole. Molecular beam conditions (80 torr, nozzle temperature = 243°K) were found where the only detectable cluster was the dimer; other beam conditions (272 torr and 246°K) were identified in which the entire series of $(CO_2)_n^+$, $1 \leq n \leq 20$, ions up to a m/z of 880 were observed. These high clusters were found to fragment at photon wavelengths only 1 eV above the m/z 88 onset, producing ions at m/z 88. Higher cluster fragmentation accounted for over 87% of the total m/z 88 signal at 20 eV photon energy.

B. Ion Intensity Calibration Through Photoionization. The complete characterization of a triple-cathode plate photoionization chamber has been accomplished, and a paper has been submitted to Analytical Chemistry. The title of the paper by A. H. Grange and J. W. Taylor is "Consideration of Design of Photoionization Chambers for Cross Section Measurements". The abstract follows:

Design parameters of photoionization chambers which influence the accuracy of cross section measurements are considered. Among these parameters are the interelectrode spacing, the nature and construction of the end plates, pressure and temperature effects, and the effective guard plate lengths. A three-cathode plate system was developed to test for deviation from assumed Beer's Law bahavior and to test designs which could provide cross section accuracies in the range ±2% for spectral regions without sharp spectral structures.

C. Calibration of Mass Spectral Ion Intensities Using Photoionization Cross Sections. A paper by Karl V. Wood, A. H. Grange, and J. W. Taylor entitled, "A Method for Calibrating a Mass Spectrometer for Mass Discrimination Effects", is in preparation, describing how we have used the absolute photoionization cross sections to calibrate the ion signals seen in our quadrupole mass spectrometer. By comparing the ratios of ion signals from a mixture inserted at low pressure in the mass spectrometer ion source to that inserted at higher pressure in the supersonic beam source, we found we could determine the amount of mass discrimination which occurs as a consequence of the beam expansion. We find the discrimination effects are a function of nozzle-skimmer distance but that at the minimum of the plot of intensity versus nozzle-skimmer distance the relationship of intensities is quite close to the square root ratios of the molecular masses, that is:

$$\frac{Intensity_{Heavy\ Species}}{Intensity_{Light\ Species}} \propto \sqrt{\frac{Mass_{Heavy\ Species}}{Mass_{Light\ Species}}}$$

We have not yet determined if this finding is a consequence of our choice of beam parameters, but if it is not, there is a ready way to determine the relationship between the ion intensities and the actual gas concentration in the high pressure source. The abstract of the paper presented to the American Chemical Society Meeting in New Orleans appears below:

Direct analytical sampling of atmospheric or sub-atmospheric pressure gases can be accomplished with a supersonic nozzle and differential pumping. Establishing a relationship between the mass spectral ion intensities and the concentrations of the species in the analytical gas requires knowledge of several mass discrimination effects. We have investigated several of these using a quadrupole mass spectrometer and photons as the ionization reagent. The mass discrimination of the quadrupole has been examined using the photoionization cross sections produced from a triple-plate ionization chamber. The mass discrimination from the beam formation has been determined by comparison of low pressure static gas mixtures and dynamic mixtures present in the nozzle chamber of the supersonic molecular beam. Several of the important criteria for analytical applications will be discussed.

D. Hydrogen Bonding Clusters in Methanol. The results of the experiments with carbon dioxide indicated that its clustering occurred as a result of cooling associated with the beam expansion process. Relative cluster intensities were observed to decrease markedly as the nozzle-skimmer distance (Z_{NS}) was decreased, presumably because the cooling process was disrupted at short Z_{NS}. By contrast, methanol clusters appeared to be present at equilibrium in the beam source. It was initially assumed that the methanol system was sampled without disruption of the equilibrium by collisions in the molecular beam expansion because a Z_{NS} variation experiment with methanol seemed to indicate an increase in relative cluster ion intensities as Z_{NS} was decreased, a trend opposite to that observed with CO_2. However, extensive background corrections were necessary to compensate for monomer scattered in the detection chamber. When this background was significantly reduced by introduction of a closed cycle helium refrigeration cryopump, it became clear that cluster ion intensities actually showed an initial decline as Z_{NS} was decreased, increasing again rapidly at very short Z_{NS}. This behavior was consistent with a model which had been suggested earlier in discussions with Professor John Fenn of Yale University. The "Fenn effect" predicts destruction of clusters in collisions near the skimmer when Z_{NS} is short enough that the skimmer disrupts the shock wave formed in the nozzle exhaust. At still shorter Z_{NS}, the shock wave is "swallowed" by the skimmer, which becomes a virtual nozzle, and the destruction of clusters abruptly ceases. This model is entirely consistent with our data for methanol. For CO_2, at low pressures (~ 100 torr), cluster ion signals were not observed to increase after the shock wave was "swallowed". This was probably because the skimmer, acting as a virtual nozzle, did not provide sufficient cooling for van der Waals clustering to take place. This confirmed the conclusion that CO_2 clusters form primarily as a result of cooling in the molecular beam expansion. At high pressure (~ 280 torr), CO_2 cluster intensities were observed to decrease only slowly as Z_{NS} was decreased, presumably because heavy clusters present at these pressures fragmented only partially, replacing some of the lighter clusters lost to collisional destruction.

Further experiments were directed at testing the assumption of methanol equilibrium. If an equilibrium existed in the molecular beam source and was not perturbed by the expansion process, the natural logarithm of the associated

equilibrium constant (as determined from relative cluster ion intensities) should display a linear van't Hoff type dependence on inverse molecular beam source temperature. Such a dependence was observed for methanol (100 torr source pressure, 25-75°C, 700 Å ionizing radiation).

In these experiments mass spectral ion signals were detected at mass to charge ratios 33, 65, 97, and 129, corresponding to the series $(CH_3OH)_n H^+$, for n = 1 to 4. (The signal at m/e 33 was significantly larger than what would be expected from the contribution from $^{13}CH_3OH$.) We have explained this observation by the following model reaction:

$$(CH_3OH)_{n-1} + CH_3OH \overset{\rightarrow}{\leftarrow} (CH_3OH)_n \overset{h\nu}{\rightarrow} (CH_3OH)_{n-1}H^+ + CH_3O\cdot + e^-$$
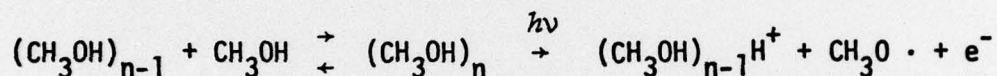
No ions of significant intensity were observed at mass to charge ratios between the ions of this series, indicating that the fragmentation pathway of the reaction is the sole fragmentation pathway for each cluster.

In these studies a great deal of effort has been expended in an attempt to assess the possibility that methanol clusters are formed as a result of cooling in the molecular beam expansion. Five specific experiments have provided suggestive, but not conclusive, evidence that clustering of methanol in the beam is not an important process. First, the observed temperature dependence of relative ion intensities is consistent with van't Hoff equilibrium behavior. Secondly, the observed dependence of cluster ion intensity on nozzle-skimmer distance, and specifically the increase of cluster intensity as the shock wave is swallowed, contrasts sharply with behavior observed with CO_2, where clusters are known to be formed primarily in the beam expansion.

A third experiment directed at determining the source of methanol clusters involved variation of the sample pressure in the molecular beam source. Cooling in the molecular beam source results from collisions in the nozzle throat. The number of these collisions, and thus the effectiveness of the cooling process, varies with the beam source pressure. Variation of methanol pressure between 20 and 100 torr was observed to effect cluster ion intensities (relative to total cluster intensity) very little.

Another property to which cooling in the molecular beam is sensitive is the composition of the expanding gas. Samples with high specific heat ratios $(C_p/C_v \equiv \gamma)$ experience more efficient collisional transfer of internal energy

to translational energy than samples of low γ. For example, CO_2 ($\gamma = 1.31$) is cooled more efficiently in the molecular beam than is methanol ($\gamma = 1.12$). When methanol vapor was diluted with CO_2 and this mixture allowed to expand from the supersonic nozzle, the cluster intensities generally increased but the temperature dependence of the cluster formation was essentially the same as for pure methanol.

The results of the beam dilution experiments have led us to consider an entirely new, "hybrid" model for methanol clustering, based on a model for rare gas association suggested recently by E. L. Knuth (J. Chem. Phys. 66, 3515 (1977)). We envision a two-step clustering mechanism whereby quasistable clusters are formed in bimolecular collisions in the molecular beam source, and subsequently stabilized in secondary two body collisions. According to this model, the great number of collisions responsible for cooling in the molecular beam expansion also results in stabilization of methanol clusters and thus the enhancement of their intensity in the molecular beam experiment. This model offers a reasonable explanation for the diluted behavior while remaining consistent with temperature, pressure, and Z_{NS} dependence data. It should be viewed at this time as an alternative explanation, rather than an answer to the methanol clustering data.

The final set of experiments to be described involved examination of some related systems. Behavior of methanol was generally reproduced in monodeuteromethanol, ethanol, and trifluoroethanol. The ion series observed for clusters of CH_3OD (m/e 33, 35, 68, 101, and 134) are consistent with the model reaction. Use of the deuterated alcohol offered the advantage of not confounding the dimer signal with the ^{13}C contribution of monomer. The temperature dependence of relative CH_3OD cluster intensities was similar, or perhaps slightly greater, than that of CH_3OH (van't Hoff plot slopes were slightly greater for the deuterated compound). If the equilibrium model is valid, this observation indicates slightly stronger hydrogen bonding in CH_3OD than in CH_3OH. Temperature dependence of ethanol was qualitatively similar to the methanol sample dependences, but again somewhat greater, indicating stronger hydrogen bonding if equilibrium exists. This conclusion is consistent with the generally accepted greater induction of the ethyl group compared to a methyl group. Results for trifluoroethanol were qualitatively

different from those for the other alcohols, in that heats of stepwise cluster formation calculated from observed temperature dependence and based on the equilibrium model did not show a smooth decline with growing cluster size, as was the case for all other alcohols. Instead, the derived heat of formation of the trimer from the dimer was considerably larger than the heat of dimerization, followed by a decrease for the heat of tetramerization (see Table I).

TABLE I

Heats of Formation ($\Delta H_{n-1,n}$, kcals/mole) of n-mers from (n-1)-mers, Estimated by Photoionization Mass Spectrometry, Assuming Equilibrium Model

Sample	Ionizing Energy (eV)	$\Delta H_{1,2}$	$\Delta H_{2,3}$	$\Delta H_{3,4}$	$\Delta H_{4,5}$
Methanol	17.7	-4.74	-2.32	-1.03	-0.25
Trifluoroethanol	12.4	-4.26	-23.46	-9.65	---

It is clear from the work described above that the question of the origin of the clustering in methanol has not yet been elucidated. However, detailed study of the system has suggested fascinating model possibilities, including the two step Knuth condensation model. The source equilibrium model remains tractable, although the observations of cluster enhancement in seeded beam experiments require consideration of mass discrimination arguments. However, the fact that our experimental heats of cluster formation based on assumed equilibrium do appear to converge toward the methanol heat of vaporization (8.8 kcals/mole at 260 torr), does suggest that the equilibrium assumption may have some validity. We are continuing to subject the model to other experiments to find the extent of its validity, and are ready to submit a draft of our data and conclusions for publication.

IV. LIST OF PRESENTATIONS OF RESEARCH RESULTS RELATED TO THIS PROJECT

Discussion and publication of research sponsored by the Office of Naval Research has occurred in the following ways as of March 31, 1977:

1. In abstract form, at the Fifth International Symposium on Molecular Beams held at Peymeinade, France, 1975, paper E-2.
2. At the VII International Conference on Photochemistry held in Edmonton, Alberta, Canada, August, 1975. The talk is abstracted in the Proceedings.
3. As part of a research paper at the Eighth Annual Synchrotron Users Group meeting held in Stoughton, Wisconsin, October, 1975.
4. At the Midwestern Universities Analytical Chemistry Conference held in Detroit, Michigan, November, 1975.
5. In J. Photochem. 5, 195 (1976).
6. As a paper by G. G. Jones and J. W. Taylor, "A Photoionization Study of Carbon Dioxide Dimers in a Supersonic Molecular Beam", J. Chem. Phys., in press.
7. As a Chemistry Department Colloquium at Michigan State University, February, 1976.
8. As part of an invited paper at the Gordon Conference on Electron Spectroscopy held in July, 1976.
9. As part of a research paper presented at the Ninth Annual Synchrotron Users Group meeting held in Stoughton, Wisconsin, October, 1976.
10. To the ONR sponsored conference on nucleation at Northwestern University, November, 1976.
11. As the Chemistry Department Colloquium at the University of Wisconsin, Oshkosh, March, 1977.
12. As a contributed paper to the American Chemical Society meeting in New Orleans, Louisiana, March, 1977.
13. As a number of Analytical Chemistry and Physical Chemistry seminars at the University of Wisconsin, Madison, Wisconsin.

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