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ROTATIONAL AND VIBRATIONAL SPECTRA OF MOLECULAR
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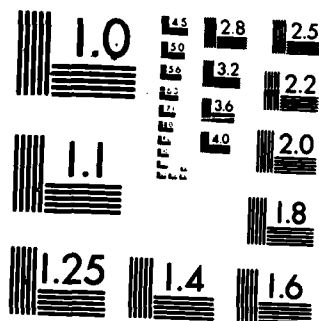
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COMPLETED PROJECT SUMMARY

TITLE: Rotational and Vibrational Spectra of Molecular Clusters

PRINCIPAL INVESTIGATOR: Professor Thomas R. Dyke
Department of Chemistry
University of Oregon
Eugene, Oregon 97403

SENIOR INVESTIGATOR: Professor Joseph W. Nibler
Department of Chemistry
Oregon State University
Corvallis, Oregon 97331

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SENIOR RESEARCH PERSONNEL: Dr. S.Y. Hou Dr. M. Maroncelli
Dr. G. Johnson

JUNIOR RESEARCH PERSONNEL: P. Herbine A. Hu
G. Pubanz G. Hopkins

PUBLICATIONS:

"Nuclear Spin Species, Statistical Weights and Correlation Tables for Weakly Bound van der Waals Complexes," K. Balasubramanian and T.R. Dyke, J. Phys. Chem. **88**, 4688 (1984).

"Microwave and Radiofrequency Spectra of Hydrogen Bonded Complexes in the Vapor Phase," T.R. Dyke, Topics in Current Chemistry, **120**, 86 (1984).

"The Microwave and Radiofrequency Spectrum of $\text{H}_2\text{S}\cdot\text{Ar}$," R. Viswanathan and T.R. Dyke, J. Chem. Phys. **82**, 1674 (1985).

"Coherent Raman Spectroscopy of HCN Complexes," G.A. Hopkins, M. Maroncelli, J.W. Nibler and T.R. Dyke, Chem. Phys. Lett. **114**, 97 (1985).

"Rotational Spectra and Structure of the Ammonia-Water Complex," P. Herbine and T.R. Dyke, J. Chem. Phys. **83**, 3768 (1985).

"Infrared and Coherent Raman Spectroscopy of HCN and DCN Dimers and Trimers," M. Maroncelli, G.A. Hopkins, J.W. Nibler, and T.R. Dyke, J. Chem. Phys. **83**, 2129 (1985).

"Molecular Beam, Infrared Absorption Studies of Rare Gas-OCS Complexes, G.D. Hayman, J. Hodge, B.J. Howard, J.S. Muentner, and T.R. Dyke, Chem. Phys. Lett. **118**, 12 (1985).

"CARS Spectra of van der Waals Complexes: The Structure of CO_2 Dimer,"

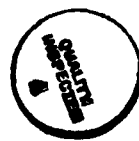
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Methods were developed for observing vibrational spectra of complexes in molecular beams using CARS. A Raman technique such as CARS has different sensitivities to various vibrational modes compared to infrared experiments and thus this research provides a powerful complement to such methods. The feasibility of using CARS was demonstrated by obtaining Raman spectra for molecular beams of HCN and DCN polymers in the CN and CH stretching regions. A force field model for the axial modes of these molecules was constructed by combining infrared and Raman data. Additionally, the infrared data supported a linear structure for HCN trimer. A similar study of CO₂ clusters in the symmetric stretching region demonstrated that the rule of mutual exclusion holds for (CO₂)₂, supporting a slipped parallel C_{2h} structure. In preliminary experiments, rotational CARS spectra of molecular beams of N₂ monomers were obtained with Raman shifts as low as a few cm⁻¹, illustrating that these methods can be extended to the low frequency intermolecular mode part of the vibrational spectrum.

In a collaborative project with B.J. Howard and J.S. Muentner, carried out at Oxford University during a sabbatical leave (T.R. Dyke), infrared absorption spectra for molecular beams of rare gas-OCS complexes in the ν_3 monomer mode region were obtained using tunable diode lasers. The spectra are rotationally resolved and the Doppler limited linewidths (0.004 cm⁻¹) show no evidence of vibrational predissociation broadening. Combination of the infrared absorption data and microwave-infrared double resonance experiments gave accurate rotational and centrifugal distortion parameters for these van der Waals molecules.



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Objectives of Project:

Intermolecular forces manifested in hydrogen bonds and van der Waals interactions largely determine the properties of many important systems such as condensed phases and macromolecules,^{1,2} and molecular clusters held together by these forces may be important in atmospheric processes.³ Our approach to studying these forces is to form molecular clusters and apply rotational and vibrational spectroscopic techniques to determine structural information for these complexes. The relatively weak binding between the constituents of such complexes ensures that large amplitude vibrational motion will occur. Therefore, to understand the structure and properties of such non-rigid systems, it is important to have both rotational and vibrational information, and the eventual goal of this research is to determine the potential energy surfaces for vibrational motion as well as the equilibrium geometries of the complexes.

The results of this work are of importance in a number of areas. In recent years there has been increasing interest in studying clusters of molecules held together by hydrogen bonds and van der Waals interactions^{4,5}. Although these interactions are quite weak, typically one-tenth to less than one-hundredth of a normal covalent bond strength¹, the large number of possible bonding arrangements gives them a dominant role in the properties of condensed phases and in macromolecule structure. Clusters involving water are of particular interest in understanding liquid water and ice, aqueous solutions and atmospheric phenomena^{2,3}. In the latter case, various water clusters have been proposed as the species giving rise to the anomalous absorption of infrared and microwave radiation in the atmosphere⁶⁻¹³. That is, it is generally found that in the vicinity

of water monomer atmospheric absorption lines, a broad, additional absorption is detected which is attributed to various sources such as water clusters, as mentioned above, or as the Lorentzian wings of the monomer lineshapes¹⁴. Our work on the rotational spectrum of $(\text{H}_2\text{O})_2$ ¹⁵⁻¹⁷ shows a very complex pattern which, under pressure broadened conditions, could well produce a nearly continuous spectrum. Some recent laboratory based measurements in the 10.4 μm infrared region have indicated that water dimers make significant contributions to atmospheric absorption below 100°C and are dominant at room temperature and below¹³. The information which we can provide is important for modelling the effects of cluster molecules in atmospheric applications as well as condensed phases and macromolecules. Ultimately it should lead to a clearer picture of hydrogen bonding and van der Waals interactions.

We have developed and employed several experimental techniques to achieve these goals. Precision structural data from pure rotational spectroscopy have been obtained by the molecular beam electric resonance technique⁴. Molecular geometries, electric dipole moments and nuclear hyperfine constants for complexes such as $(\text{H}_2\text{O})_2$ ¹⁷, $\text{NH}_3 \cdot \text{H}_2\text{O}$ ¹⁸ and others have been found from these experiments. We have pioneered experiments utilizing coherent Raman methods such as CARS for determining vibrational spectra of molecular beams of hydrogen bonded and van der Waals complexes such as HCN clusters^{19,20} and CO_2 ²¹ clusters. In addition, quite recently we have developed diode laser techniques for observing infrared absorption spectra for weakly bound complexes in molecular beams²²⁻²⁴, in a collaborative project with B.J. Howard (Oxford University) and J.S. Muentert (University of Rochester). In the following section of this report, the experimental methods and significant results of this work will be briefly

discussed.

Current Status and Results of Project

Rotational Spectroscopy of Complexes:

Radiofrequency and microwave spectroscopy of molecular complexes were obtained using the molecular beam electric resonance method^{4,25,26}. In these experiments, the complexes were produced in a free-jet expansion with an argon carrier gas to achieve low translational and rotational temperatures. After leaving the molecular beam source chamber, the complexes were rotationally state selected and focused with two 50 cm long, electrostatic quadrupole fields of 0.48 cm aperture. Electric dipole transitions were induced in the resonance region between the two quadrupole fields with radiofrequency and microwave radiation between 0-40 GHz. After passing through the state selection and resonance fields, the beam molecules were detected by a mass spectrometer with a Weiss type ionizer and 60° sector magnet mass analyzer.

The observed linewidths depended primarily on the transit time of the molecules through the resonance field, which is 25 cm long, giving 3 kHz widths at radiofrequencies and 20 kHz at microwave frequencies from residual Doppler effects. From the resulting high resolution spectra, precision rotational constants can be found from microwave transitions and structures calculated from data for different isotopic species. From radiofrequency spectra ($\Delta J=0$, $\Delta M_J = 1$ transitions), accurate electric dipole moments and nuclear hyperfine interaction constants are determined. Comparison of these quantities with their counterparts for the free monomers provides useful information concerning the monomer orientation in the complex, or concerning changes in the monomer charge distribution upon

forming a complex. The accurate rotational frequencies from the microwave spectrum also supply centrifugal distortion constants, which contain useful information concerning the vibrational potential. The results of these experiments are discussed below.

The $(\text{H}_2\text{O})_2$ molecule is a particularly important hydrogen bonded molecule for understanding a variety of condensed phase and atmospheric phenomena, as mentioned above. We have continued our studies^{15,16} of the microwave spectrum of this molecule and have finished a series of measurements on the $K = 0$ spectra of $(\text{H}_2\text{O})_2$ and $(\text{D}_2\text{O})_2$. This work¹⁷ has shown that the a-type spectra have series of transitions which are split by large tunneling doublings, 19,527 MHz for $(\text{H}_2\text{O})_2$, in addition to series of lines which do not show tunneling splittings. The frequencies are given in Table 1 and the molecular constants in Table 2. These results may shed some light on the atmospheric anomalous absorption problem, in that the tunneling splittings greatly enrich the microwave spectrum of this molecule. Additionally, the splittings are likely to be substantially different in excited vibrational states. Thus the vibration-rotation spectrum of this species will be very dense and, with pressure broadening, could present a nearly continuous spectrum. In this regard, it will be important to observe spectra for higher polymers of water which could also contribute and some effort will be directed toward studying trimers. An accurate structure for $(\text{H}_2\text{O})_3$ has not been experimentally determined and the questions of cyclic vs. chain structures^{27,28} and cooperative effects are important.

The structure of $\text{NH}_3 \cdot \text{H}_2\text{O}$ has been determined during this project¹⁸ from the rotational constants and nitrogen quadrupole coupling constants for this species and partially deuterated forms, and the results are shown

Table 1
Water Dimer K=0 Frequencies

Transition J → J'	Frequency (MHz)
--- (H ₂ O) ₂ ---	
2 ⁺ → 1 ⁻	4863.16
0 ⁻ → 1 ⁺	7354.86
1 → 0	12132.70
1 ⁻ → 0	12321.00
3 ⁺ → 2 ⁻	17122.61
2 ⁻ → 1 ⁻	24640.88
4 ⁺ → 3 ⁻	29416.39
--- (D ₂ O) ₂ ---	
1 ⁺ → 0 ⁻	9692.87
1 → 0	10864.58
1 ⁻ → 0 ⁺	10864.54
1 ⁻ → 0 ⁺	12036.70
1 ⁻ → 2 ⁺	20557.43

Table 2. Water Dimer Molecular Constants (in MHz)

Type of Spectrum	(B+C)/2	ν	a	δ	D _J
---(H ₂ O) ₂ ---					
E	6160.50	0	0	0	0.04
E	6066.40	0	0	0	-
A/B	6073.98	19526.80	-24.34	0.10	-
---(D ₂ O) ₂ ---					
E	5432.29	0	0	0	-
E	5432.27	0	0	0	-
A/B	5432.36	1172.65	-0.48	-	-
A/B	(5432)	(2150)	-	-	-

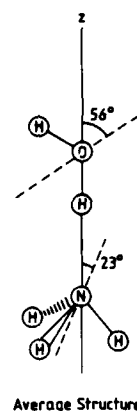
$$W = \frac{1}{2}(B+C)J(J+1) - D_J J^2(J+1)^2 \pm [\nu/2 + aJ(J+1) + \delta J^2(J+1)^2]$$

in Table 3. This molecule has a linear (or nearly linear) hydrogen bond and the $O \cdots H-N$ distance of 2.98 Å is of particular interest since it is identical to the $O \cdots O$ distance in water dimer. The similarity holds in condensed phases as well, since both ice and the $2NH_3 \cdot H_2O$ crystal have 2.84 Å heavy atom separations^{1,29}. This similarity is quite surprising. Electron pair donor-acceptor models have been used to explain the structures of hydrogen bonded complexes. However, in such a model, NH_3 would be expected to be a better electron donor than H_2O , resulting in a stronger and shorter hydrogen bond than for $(H_2O)_2$. That this is not the case suggests that these models may not be useful in predicting hydrogen bond strength, or that the hydrogen bond length is not a good indicator of relative strength. In addition, no evidence for proton transfer, such as an unusually large electric dipole moment or small nitrogen quadrupole coupling constant was observed.

For comparison with the $NH_3 \cdot H_2O$ and water dimer work, $NH_3 \cdot H_2S$ and $H_2O \cdot H_2S$ are being studied. Work on the $H_2O \cdot H_2S$ molecule has just begun; however the $NH_3 \cdot H_2S$ structure has been determined³⁰ and the results are given in Table 4. The structure is very similar to $NH_3 \cdot H_2O$, although the hydrogen bond is about 0.3 Å longer. Again, there is no indication of proton transfer, although naively H_2S would be expected to be a better proton donor than H_2O . One rather novel observation for this molecule is that in $K = 1$ states it shows linear Stark effects at all electric fields employed and for $J = 1-9$, despite the fact that it is an asymmetric rotor and should have quadratic Stark effects. However, if the barrier to ammonia internal rotation is less than about 900 cm^{-1} , we have calculated that symmetric rotor, linear Stark effect behavior will be observed. I.e. in the low barrier limit, states correlating with NH_3 free rotor levels

Table 3. Structural data for $\text{NH}_3 \cdot \text{H}_2\text{O}$

$R(\text{N} \cdots \text{H}-\text{O})/\text{\AA}$	2.983
$R(\text{N} \cdots \text{D}-\text{O})/\text{\AA}$	2.979
$\theta'_\text{N}(\text{NH}_3 \cdot \text{H}_2\text{O})/\text{deg}$	23.1 (2)
$\theta'_\text{N}(\text{ND}_3 \cdot \text{D}_2\text{O})/\text{deg}$	20.4 (5)
$\theta_\text{O}/\text{deg}$	56
χ_O/deg	~ 0
$\omega_\text{N}/\text{cm}^{-1}$	168 (3)
$k_\text{N}/\text{mdyne}/\text{\AA}$	0.145 (5)

Table 4. Structural Data for $\text{NH}_3 \cdot \text{H}_2\text{S}$

$R(\text{N} \cdots \text{H}-\text{S})/\text{\AA}$	3.634
$\theta'_\text{N}/\text{deg}$	24.0
$\theta'_\text{S}/\text{deg}$	47.3
$\chi_\text{S}/\text{deg}_1$	0
$\omega_\text{S}/\text{cm}^{-1}$	104
$k_\text{S}/\text{mdyne} \cdot \text{\AA}$	0.072

Table 5.

Structural parameters for $\text{H}_2\text{S} \cdot \text{Ar}$, $\text{HDS} \cdot \text{Ar}$, and $\text{D}_2\text{S} \cdot \text{Ar}$. The effective parameters given below are defined from various observed quantities, as discussed in the text.

	$\text{H}_2\text{S} \cdot \text{Ar}$		$\text{HDS} \cdot \text{Ar}$		$\text{D}_2\text{S} \cdot \text{Ar}$	
$R(\text{\AA})^a$	3.977 (2)		3.958 (3)		3.921 (4)	
$\langle \cos \theta \rangle^b$	0.187 (30)		0.194 (30)		0.221 (30)	
$\langle \cos^2 \gamma_{\text{HH}} \rangle$	0.670 (11)		...		...	
$\omega, (\text{cm}^{-1})$	22.2 (2)		22.4 (2)		24.7 (2)	
$k, (\text{mydn} \cdot \text{\AA}^{-1})$	0.0053 (1)		0.0055 (1)		0.0068 (1)	
	Acute	Obtuse	Acute	Obtuse	Acute	Obtuse
	$\text{H}_2\text{S} \cdot \text{Ar}$		$\text{HDS} \cdot \text{Ar}$		$\text{D}_2\text{S} \cdot \text{Ar}$	
$\gamma_{\text{HH}} (\text{deg})$	35.1	144.9 (1.0)	...	...	...	...
$\theta' (\text{deg})^b$	79.2	100.8 (2.0)	78.8	101.2 (2.0)	77.2	102.8 (2.0)
$\chi' (\text{deg})^c$	33.6	146.4 (1.5)	27.2	152.8 (3.0)	...	...
$R_{\text{As}} (\text{\AA})$	3.967	3.988	3.919	3.999	3.899	3.945

^a Errors quoted assume $\pm 15^\circ$ uncertainty in angular geometry.

^b Errors quoted reflect uncertainty in induced moment calculation.

^c $\chi' = \chi'_\text{H}$ for $\text{H}_2\text{S} \cdot \text{Ar}$ and χ'_D for $\text{HDS} \cdot \text{Ar}$.

will behave like a symmetric top, giving the observed linear Stark effects and absence of K-doubling. We are currently re-investigating the $\text{NH}_3 \cdot \text{H}_2\text{O}$ spectrum for such effects since the presumably higher barrier to internal rotation for this species and for the fully deuterated analog (which is easier to produce than $\text{ND}_3 \cdot \text{D}_2\text{S}$) may allow the barrier height to be accurately calculated rather than only an upper limit placed.

It is quite important to point out that the $\text{NH}_3 \cdot \text{H}_2\text{S}$ internal rotation result and the water dimer tunneling doubling result show clearly that tunneling effects are pervasive in hydride-complexes with permutation symmetry, even though the a-type microwave spectrum may appear to be that of a rigid rotor. Several years ago we found that all transitions in the a-type rotational spectrum for $(\text{HF})_2$ were split by a tunneling doubling of 19,747 MHz^{25,31}. For monomer constituents more complex than linear molecules, the above results show that a "normal" a-type spectrum does not preclude large-amplitude tunneling motions from occurring. The vibrational spectra of these molecules may be very complex because of these motions, and the pure rotational spectroscopy done here and in other labs for these complexes may be crucial in achieving assignments.

Some work is in progress to look at very weak complexes such as $\text{Ar} \cdot \text{H}_2\text{O}$, $\text{N}_2 \cdot \text{H}_2\text{O}$ and $\text{H}_2\text{S} \cdot \text{Ar}$. The $\text{H}_2\text{S} \cdot \text{Ar}$ rotational spectrum has been studied³² and the results are quite interesting in that the molecule does not appear to be hydrogen bonded (Table 5). Extensive work by others on inert-gas, hydrogen halide complexes³³ has suggested linear equilibrium structures with the hydrogen halide pointing towards the inert gas. The $\text{H}_2\text{S} \cdot \text{Ar}$ work suggests that induction and dispersion forces may well be the dominant intermolecular forces holding these weak complexes together, and that a unique "hydrogen bonding" description is not applicable to these

complexes, even though the inert-gas, hydrogen halide complexes have a hydrogen bonded geometry. Comparisons with $\text{Ar}\cdot\text{H}_2\text{O}$, $\text{N}_2\cdot\text{H}_2\text{O}$ and related complexes will be interesting in this regard.

Vibrational Spectroscopy of Complexes:

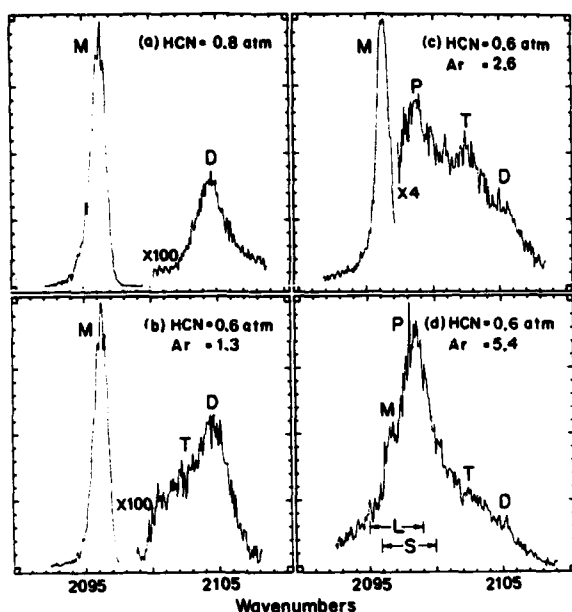
In this project, we have observed CARS spectra for molecular beams of $\text{HCN}^{19,20}$ and CO_2 clusters²¹, as illustrated by Figures 1 - 3. This represents the first detailed spectroscopic study of such complexes by coherent Raman methods. It is gratifying that the sensitivity has proven sufficient to detect dimer species at very low dilution ratios (1% as in Fig. 3) and relatively large X/D distances (~ 15). The success of this work is quite encouraging and demonstrates that coherent Raman techniques will be productive for this research. In what follows, the current apparatus at Oregon State University will be briefly described along with a discussion of our results.

The vibrational CARS spectra shown in Figures 1 - 3 were taken with a Quanta-Ray Nd/YAG laser which provided a 532 nm pump beam consisting of 10 nsec pulses with 0.02 cm^{-1} width, $\sim 70 \text{ mJ}$ energy and 10 Hz repetition rate. Half the output was used to pump a Quanta-Ray PDL-1 tunable dye laser with 0.3 or 0.05 cm^{-1} resolution modes. The pump and Stokes beams were spatially separated and focused (300 mm focal length lenses) with a crossing angle of $\sim 1^\circ$ at the jet position. Since the phase matching condition,³⁴

$$\vec{k}_3 = 2\vec{k}_1 - \vec{k}_2$$

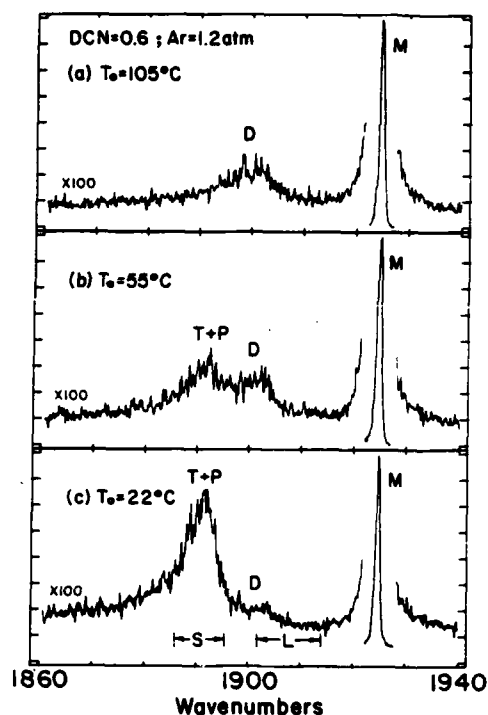
is no longer exact, some loss of CARS signal results. However, the coherence length at this small crossing angle is roughly 0.5 cm, compared

Figure 1



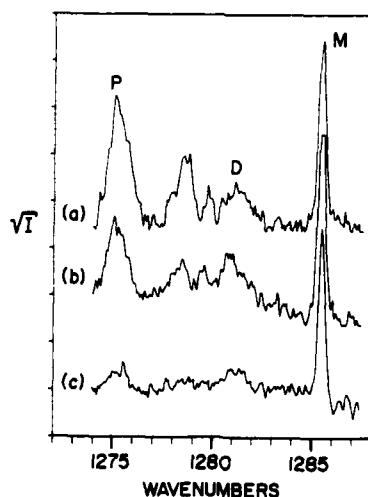
CARS spectra of the ν_1 region of HCN in supersonic expansions of HCN/Ar mixtures. Peaks are labeled as M = monomer, D = dimer, T = trimer, and P = higher polymers. All spectra were recorded under similar expansion conditions ($T_0 = 300$ K, $X/D = 1$, $D = 0.13$ mm) except for the addition of successively higher pressures of Ar driving gas (b)-(d). In spectrum (d) the regions labeled S and L denote the position and FWHH of ν_1 in solid (78 K) and liquid (261 K) HCN (Ref.40).

Figure 2



CARS spectra of the ν_1 region of a 1:2 DCN/Ar expansion showing the effect of variations in the nozzle temperature T_0 . S and L show the frequencies observed for solid and liquid DCN (Ref. 40).

Figure 3



The effect of concentration and pressure on the distribution of cluster sizes. (a) $\%CO_2 = 5$, $X/D = 2.1$, $T_0 = 208$ K, $P_0 = 12$ atm. (b) $\%CO_2 = 2$, $X/D = 2.0$, $T_0 = 208$ K, $P_0 = 14.6$ atm. (c) $\%CO_2 = 1$, $X/D = 1.8$, $T_0 = 208$ K, $P_0 = 18$ atm.

to an approximately 0.1 cm long region at the focus which generates most of the CARS signal. Thus the reduction in signal is not severe and the signal-to-noise ratio is actually improved by the greater discrimination against nonresonant scattering in the input lens and molecular beam chamber windows. The expansion chamber contained a pulsed nozzle molecular beam source. Pump and Stokes energies at the sample were typically 1-3 mJ per pulse respectively. After the cell, the beams were recollimated and the CARS signal was isolated with a dichroic mirror and one or more optical glass filters. It was then sent into a 0.3 m McPherson monochromator for further rejection of the 532 nm light and was detected with a photomultiplier. After preamplification and gated integrator processing, the output was averaged for 10-50 shots and stored in a DEC Micro-11 computer controlling the experiment.

For the initial work, HCN was chosen for the relative simplicity of the linear molecule monomer spectrum, and additionally, some aspects gas phase hydrogen bonding in HCN are well known. Extensive vapor density data has been taken and the thermodynamics of cluster formation analyzed³⁵. The rotational spectrum and structure of the dimer has been determined³⁶. Although a substantial amount of matrix isolation infrared work has been reported (see reference 20 for a listing of articles), the only gas phase vibrational data for HCN polymers is a single gas phase dimer band in the CN stretching region of the infrared spectrum³⁷. In this work, Raman spectra for HCN and DCN polymers were observed in the monomer CH and CN stretching regions using the CARS technique in conjunction with a molecular beam source^{19,20}. In addition, supplementary data was obtained using PARS (photoacoustic Raman spectroscopy) and Fourier transform infrared techniques on static gas samples.

Sample spectra are shown in Figures 1 and 2 illustrating the ability to select the amount of clustering by varying the nozzle source temperature and stagnation pressure. The frequency data from these experiments is summarized in Table 6 and a force constant model used to describe the frequencies and intensities is given in Tables 7 and 8. These results are discussed in detail in reference 19 and 20. The principal findings include the observations that the observed frequencies and the force constants derived from them show that very little perturbation of the CN bond results from hydrogen bonding, consistent with the results of ab initio calculations³⁸⁻⁴⁰. As expected, the bonded CH stretch is much more affected. The 6% change in diagonal force constant and the dipole derivative increase implied by the 30-fold IR intensity enhancement of ν_1 are indicative of a substantial perturbation of the CH bond.

All evidence indicates that the hydrogen bonds are stronger in the trimer than in the dimer. The CH frequency shifts of the trimer are larger, approaching those of solid HCN where the hydrogen bond lengths are significantly shorter than the gas phase dimer value. The IR ν_1 intensity enhancement relative to the monomer is much greater in the trimer (~500) than in the dimer (~30), indicating a greater electronic change in the CH bond. The trimer enhancement factor is very similar to the corresponding solid/gas cross section ratio of ~490⁴¹, suggesting a similarity to the solid.

One of the interesting aspects of the present work is the identification of the HCN trimer. The rotational envelope observed for the IR ν_1 trimer mode provides convincing evidence for a linear structure. Other, less direct, vibrational predissociation results on $(\text{HF})_3$ ⁴² and $(\text{H}_2\text{O})_3$ ⁴³ and their higher polymers, as well as electric deflection studies

Table 6

Summary of observed frequencies.*

Frequency (cm ⁻¹)	Shift (cm ⁻¹)	FWHH (cm ⁻¹)	Method; conditions	Assignment
DCN ν_1 region				
1890.5 $\pm$ 0.5	- 34.7	7.9 $\pm$ 0.4	CARS ; 100 K	<i>T</i> (+ <i>P</i>)
1900.3 $\pm$ 0.5	- 24.9	11 $\pm$ 1	CARS ; 150 K	<i>D</i> (+ <i>T</i> ?)
1925.2	...	...	Ref. 31 ; 293 K	<i>M</i>
HCN ν_1 region				
2094.7 $\pm$ 0.3	- 2.1	18 $\pm$ 3	IR ; 293 K	<i>D</i>
2096.8	...	...	Ref. 31 ; 293 K	<i>M</i>
2098.6 $\pm$ 0.5	+ 1.8	2.8 $\pm$ 0.5	CARS ; 100 K	<i>P</i>
2100.2 $\pm$ 0.5	+ 3.4	14 $\pm$ 1	IR ; 293 K	<i>T</i>
2102.1 $\pm$ 0.5	+ 5.3	2.6 $\pm$ 0.3	CARS ; 150 K	<i>T</i>
2104.6 $\pm$ 0.3	+ 7.8	2.6 $\pm$ 0.3	CARS ; 150 K	<i>D</i>
HCN ν_2 region				
3143.9 $\pm$ 0.6	- 167.6	54 $\pm$ 4	CARS ; 100 K	<i>P</i>
3160 $\pm$ 6	- 152	73 $\pm$ 7	CARS ; 150 K	<i>T</i> (+ <i>P</i> ?)
3246 $\pm$ 15	- 65	~60	CARS ; 150 K	<i>D</i> (?)
3311.5	...	...	Ref. 31 ; 293 K	<i>M</i>

*The CARS frequencies and their associated errors refer to the band maxima which may differ from the actual ν_0 ($J = 0 \leftarrow J = 0$) by $\pm$ (FWHH/2).

Table 7

Harmonic stretching force constants (N/M) for HCN complexes.*

- 21.1					
H-C≡N					
624.4	1871				
- 34.5 - 34.5					
H-C ≡ N-----H-C ≡ N					
(624.4)	1894	(11)	586.9	(1871)	
(- 34.5) (- 34.5) (- 34.5)					
H-C ≡ N-----H-C ≡ N-----H-C ≡ N					
(624.4)	(1894)	(11)	553.8	1896	(11) (586.9) (1871)

*The CH-CN interaction constant is shown above, the bond stretching constants below the structure. Values shown in parentheses were held fixed.

Table 8

Summary of normal coordinate calculations.

Harmonic frequency (cm ⁻¹)	Calculated frequency (cm ⁻¹)	Shift D-M,T-M (cm ⁻¹)	Infrared intensity (Calc.)	Raman intensity (Calc.)	Mode description (PED %)
HCN					
3441.2	3441.2	...	100	23	CH(95) - CN(5)
2128.7	2128.7	...	0.1	100	CN(94) + CH(6)
DCN					
2703.3	2703.3	...	51	1	CD(68) - CN(32)
1952.1	1952.1	...	5	91	CN(67) + CD(33)
HCN[1]-HCN[2]					
...	3452.0	+ 10.9	98	21	CH1(94)
3376.2	3376.0	- 65.1	102	22	CH2(93)
2136.5	2136.7	+ 8.0	0.3	143	CN1(89)
2126.6	2122.6	- 6.1	0.2	60	CN2(88)
...	116.3	...	...	...	HB(98)
DCN[1]-DCN[2]					
...	2724.5	+ 21.2	48	1	CD1(66) + CN1(33)
...	2673.8	- 29.5	53	2	CD2(63) - CN2(36)
...	1950.9	- 1.3	8	123	CN1(63) + CD1(33)
1927.2	1929.4	- 22.7	4	57	CN2(61) + CD2(35)
...	114.3	...	...	...	HB(98)
HCN[1]-HCN[2]-HCN[3]					
...	3452.0	+ 10.9	99	21	CH1(94)
...	3376.0	- 65.1	98	21	CH3(92)
3289.2	3289.7	- 151.4	103	20	CH2(91)
2134.0	2138.1	+ 9.4	0.6	223	CN1(64) + CN2(27)
2132.1	2131.7	+ 3.0	0.2	24	CN2(58) - CN1(29)
...	2121.5	- 7.2	0.1	59	CN3(86)
...	142.6	...	...	...	HB1 - HB2
...	82.2	...	...	...	HB1 + HB2
DCN[1]-DCN[2]-DCN[3]					
...	2724.5	+ 21.1	50	1	CD1(66) - CN1(33)
...	2673.6	- 29.7	46	2	CD3(63) - CN3(36)
...	2635.2	- 68.1	54	4	CD2(58) - CN2(41)
...	1950.6	- 1.5	8	117	CN1(64) + CD1(34)
...	1930.4	- 21.7	10	122	CN3(59) + CD3(33)
1917.4	1915.6	- 36.5	3	30	CN2(53) + CD2(38)
...	140.2	...	...	...	HB1 - HB2
...	80.7	...	...	...	HB1 + HB2

for a number of species⁴⁴ point to cyclic structures for small n -mers with $n \geq 3$. HCN is somewhat unique in that the electron donating group is an sp hybridized lone pair. For a cyclic geometry, the s orbital of the hydrogen atom would have poorer overlap with such a lone pair and it is reasonable that the linear trimer should be preferred, even at the expense of one extra, but weaker, hydrogen bond.

A second study conducted under this project involved the structure of the CO_2 dimer²¹, which has been the subject of considerable research, including static gas cell⁴⁵ and matrix⁴⁶ infrared work, electric deflection^{47,48} and infrared laser vibrational predissociation spectroscopy⁴⁹. Despite this effort, the dimer conformation has been a matter of some controversy. In our work, the CARS spectrum of CO_2 clusters in a molecular beam was examined in the ν_1 region (Figure 3). Comparison of this result with the gas phase infrared spectrum has shown that the rule of mutual exclusion is operative for CO_2 dimer. Thus an offset parallel C_{2h} structure is supported by this experiment. This work also illustrates the usefulness of having available complementary techniques such as Raman and infrared methods, since their differing sensitivities allow a maximum amount of information to be gained.

These successes have demonstrated the power of applying coherent Raman techniques to the spectroscopy of weakly bound complexes and a substantial amount of information has been obtained in this work. It is clear, however, that considerably more information will be found by improving the resolution and extending the frequency range down to the intermolecular mode region, typically below 500 cm^{-1} . To improve the resolution to about 0.002 cm^{-1} , we plan to use pulse amplified cw lasers to provide the necessary power for CARS experiments while retaining the frequency

stability (within the pulse transform limit) and single mode character of cw lasers. In preliminary experiments on static samples, this level of resolution has been achieved. It is important to note that since the peak CARS signal is proportional to $\Delta\nu^{-2}$, substantial gains in Raman scattering intensity will also be achieved.

For the second improvement, extending the CARS experiments to low frequencies, rejection of pump and Stokes beams is a severe problem at small Raman shifts. In the last few months we have been able to overcome this problem using a folded BOXCAR⁵⁰ arrangement in which the pump beam is split into two components which are crossed at the sample in a plane perpendicular to the Stokes beam. This three dimensional phase matching scheme obviates the need for collinear beams and provides a method for spatially separating the CARS signal from the source beams. By adding a spatial filter and polarization rejection of part of the background light, excellent spectra have been obtained for N₂ jets down to zero shift (Fig. 4). Thus the low frequency region is now accessible by these methods and this capability will be used to probe low frequency Raman active vibrational modes and to obtain pure rotational Raman data, a feature of special interest for nonpolar aggregates.

In addition to the coherent Raman techniques which we have developed, we will briefly describe some important results concerning infrared absorption spectroscopy of van der Waals complexes in molecular beams. In work at Oxford University while one of us was on sabbatical leave (T.R. Dyke, AY '84-85), and in collaboration with B.J. Howard and J.S. Muentert, we have developed techniques utilizing tunable infrared diode lasers to obtain absorption spectra of these molecules.²²⁻²⁴ This method appears to be a powerful one, as illustrated in Figs. 5 and 6 which show infrared

Figure 4. Low frequency CARS spectra of neat N_2 jets. $T_0=300K$, $P_0=10$ atm, $D=0.25$ mm.

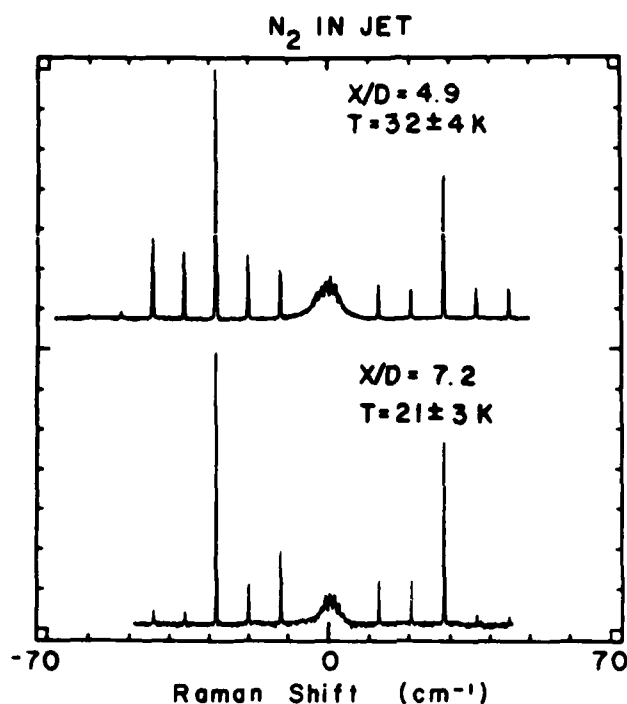
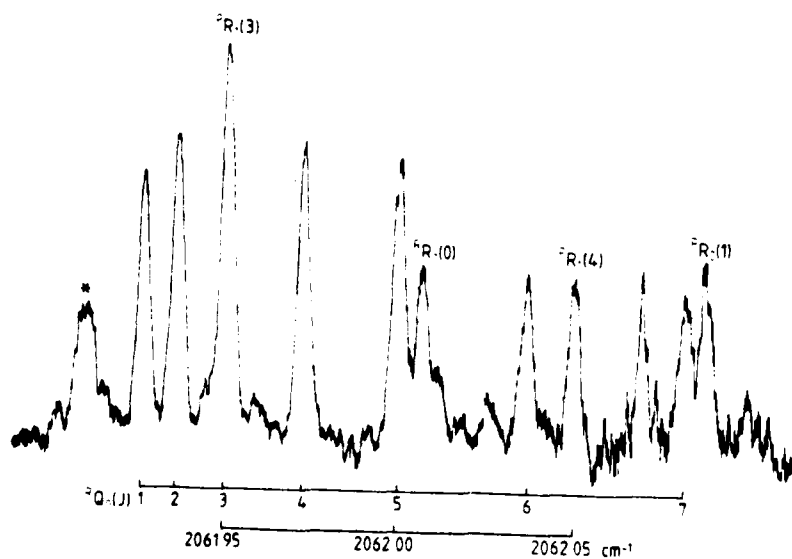


Figure 5



Ar-OCS RQ_0 band in the OCS ν_3 region, with an effective 10 s observation time constant. Note (i) that the $RQ_0(3)$ and the $PR_1(3)$ lines are virtually coincident; (ii) * indicates the $R(6)$ monomer ν_3 hot band with one quantum of ν_1 excitation.

Table 9

	Infrared and Microwave Transitions	Infrared Transitions Only
ν_o/cm^{-1}	2062.3158(3)	2062.3157(4)
A'/MHz	7296.6(3.7)	7294.6(43)
B'	2551.9(10)	2547.8(24)
C'	1860.5(14)	1858.9(17)
A''	7363.36(9)	7361.0(72)
B''	2552.94(5)	2548.9(24)
C''	1866.43(4)	1863.1(21)
D _J /kHz	78.3(8)	
D _{JK}	-74(9)	
D _K	1.853(16)	
d ₁	-29.8(14)	
d ₂	-1.3(20)	

Figure 6. Ne-OCS double resonance of the $R_{Q_0}(2)$ infrared transition with the $3_{13} - 2_{02}$ rotational transition of the ground vibrational state.



absorption and microwave infrared double resonance spectra.

In these experiments, pulsed molecular beams are used to provide high-pressure free-jet expansions which are useful for forming even very weak complexes such as the Ne-OCS complex in Fig. 6. In addition, gated detection of the infrared beam provides substantial reduction in the effects of laser 1/f noise and a consequent gain in signal-to-noise ratios. The infrared beam is passed transversely through the molecular beam, typically with substantial multi-passing, and then exits to the detector. The sampling is arranged close enough to the nozzle orifice ($X/D \sim 30-50$) to provide a high enough density of absorbers, but far enough away to provide rotational cooling to ~ 1 K, as evidenced in Fig. 5, with consequent good signal-to-noise ratios and simplification of spectra. The linewidths are then Doppler-limited to roughly 120 MHz (0.004 cm^{-1}), depending on the collimation of the molecular beam.

For cases where higher accuracy is necessary, e.g. to determine centrifugal distortion constants, we have shown that microwave-infrared double resonance experiments are possible, and linewidths as narrow as ~ 200 kHz achieved (Figure 6 and Table 9). These double resonances experiments depend on the thermal population inequality in the jet expansion source, and are confined to the vibrational ground state. It should be possible to extend this method to the upper state in the infrared transition, giving more extensive spectroscopic information and also increasing the lifetime region probed in experiments aimed at van der Waals molecule predissociation dynamics.

Conclusion

In the above discussion, we have reported the results of our research

using rotational and vibrational spectroscopy of weakly bound complexes and the developement of powerful probing techniques for obtaining vibrational spectra of complexes in molecular beams. The results of this work and future research building upon it will make important contributions toward determining the potential energy surfaces of weakly bound complexes and should lead to important insights concerning intermolecular forces.

References

1. G.C. Pimentel and A.L. McClellan, 'The Hydrogen Bond', (Freeman, San Francisco, 1960).
2. 'Water, A Comprehensive Treatise', F. Franks, ed., (Plenum, New York, 1972).
3. 'Atmospheric Water Vapor', A. Deepak, T.D. Wilkerson, and L.H. Ruhnke, eds., (Academic, New York, 1980).
4. T.R. Dyke, Topics in Current Chemistry 120, 86 (1984).
5. A.C. Legon, Ann. Rev. Phys. Chem. 34, 275 (1983).
6. D.T. Llewellyn Jones, R.J. Knight, and H.A. Gebbie, Nature 274, 876 (1978).
7. W.R. Watkins, K.O. White, L.R. Bower, and B.Z. Sojka, Appl. Optics 18, 1149 (1979).
8. L.S. Bernstein, P.C. Robertson, J.A. Covant, and B.P. Sandford, Appl. Optics 18, 2454 (1979).
9. H.R. Carlon, Appl. Optics 17, 3192 (1978).
10. H.R. Carlon and C.A. Harden, Appl. Optics 19, 1776 (1980).
11. S.H. Suck, J.L. Kassner, Jr. and Y. Yamaguchi, Appl. Optics 18, 2609 (1979).
12. S.H. Suck, A.E. Wetmore, T.S. Chen, and J.L. Kassner, Jr., Appl. Optics 21, 1610 (1982).
13. G.L. Loper, M.A. O'Neill, and J.A. Gelbwacks, Appl. Optics 22, 3701 (1983).
14. S.A. Clough, F.X. Kneizys, R. Davis, R. Gamache, and R. Tipping,

in ref. 3.

15. T.R. Dyke, R.M. Mack, and J.S. Muentner, J. Chem. Phys. 66, 498 (1977).
16. J.A. Odutola and T.R. Dyke, J. Chem. Phys. 72, 5062 (1980).
17. G. Johnson, J.A. Odutola, D. Prinslow, and T.R. Dyke. To be published.
18. P. Herbine and T.R. Dyke, J. Chem. Phys. 83, 3768 (1985).
19. G.A. Hopkins, M. Maroncelli, J.W. Nibler, and T.R. Dyke, Chem. Phys. Lett. 114, 97 (1985).
20. M. Maroncelli, G.A. Hopkins, J.W. Nibler, and T.R. Dyke, J. Chem. Phys. 83, 2129 (1985).
21. G.A. Pubanz, M.P. Maroncelli and J.W. Nibler, Chem. Phys. Lett. 120, 313 (1985).
22. G.D. Hayman, J. Hodge, B.J. Howard, J.S. Muentner, and T.R. Dyke, Chem. Phys. Lett. 118, 12 (1985).
23. G.D. Hayman, J. Hodge, B.J. Howard, J.S. Muentner, and T.R. Dyke. In preparation.
24. G.D. Hayman, J. Hodge, B.J. Howard, and T.R. Dyke, Trans. Faraday Soc. In press.
25. T.R. Dyke, B.J. Howard, and W. Klemperer, J. Chem. Phys. 56, 2442 (1972).
26. R. Viswanathan and T.R. Dyke, J. Chem. Phys. 77, 1166 (1982).
27. J. Del Bene and J.A. Pople, J. Chem. Phys. 55, 2296 (1971).
28. B. Lentz and H. Scheraga, J. Chem. Phys. 58, 5296 (1973).
29. W.J. Siemons and D.H. Templeton, Acta Crystallogr. 7, 194 (1954).
30. P. Herbine, G. Johnson, A. Hu and T.R. Dyke. To be published.
31. B.J. Howard, T.R. Dyke and W. Klemperer, J. Chem. Phys. 81, 5417 (1984).
32. R. Viswanathan and T.R. Dyke, J. Chem. Phys. 82, 1674 (1985).
33. See ref. 4 for a listing of references.
34. J.W. Nibler and G.V. Knighton, Topics in Current Physics, A. Weber, ed. (Springer Verlag, New York, 1979) Vol. 11.
35. W.F. Giaque and R.A. Ruehrwein, J. Am. Chem. Soc. 61, 2626 (1939).
36. E.J. Campbell and S.G. Kukolich, Chem. Phys. 76, 225 (1983).

37. I.R. Dagg and H.W. Thompson, Trans. Faraday Soc. 52, 455 (1956).
38. A. Karpfen, Chem. Phys. 79, 211 (1983).
39. B.A. Pettit, R.J. Boyd and K.E. Edgecombe, Chem. Phys. Lett. 89, 478 (1982).
40. S. Schreiner, Theor. Chim. Acta (Berl) 57, 71 (1980).
41. H.B. Friedrich and P.F. Krause, J. Chem. Phys. 59, 4942 (1973).
42. J.M. Lisy, A. Tramer, M.F. Vernon and Y.T. Lee, J. Chem. Phys. 75, 4733 (1981).
43. M.F. Vernon, D.J. Krajnovich, H.S. Kwok, J.M. Lisy, Y.R. Shen and Y.T. Lee, J. Chem. Phys. 77, 47 (1982).
44. J.A. Odutola, R. Viswanathan and T.R. Dyke, J. Am. Chem. Soc. 101, 4787 (1979). T.R. Dyke and J.S. Muentert, J. Chem. Phys. 57, 5011 (1972).
45. L. Mannik, J.C. Stryland and H.L. Welsh, Can. J. Phys. 49, 3056 (1979).
46. L. Fredin, B. Nelander and G. Ribbegard, J. Mol. Spectrosc. 53, 410 (1974).
47. A.E. Barton, A. Chablo and B.J. Howard, Chem. Phys. Lett. 60, 414 (1979).
48. S.E. Novick, P.B. Davies, T.R. Dyke and W. Klemperer, J. Am. Chem. Soc. 95, 8547 (1973). J.M. Lobue, J.K. Rice and S.E. Novick, Chem. Phys. Lett. 112, 376 (1984).
49. T.E. Gough, R.E. Miller and G. Scoles, J. Phys. Chem. 85, 4041 (1981).
50. A.C. Eckbreth, Appl. Phys. Lett. 32, 421 (1978).

Publications:

"Nuclear Spin Species, Statistical Weights and Correlation Tables for Weakly Bound van der Waals Complexes," K. Balasubramanian and T.R. Dyke, J. Phys. Chem. **88**, 4688 (1984).

"Microwave and Radiofrequency Spectra of Hydrogen Bonded Complexes in the Vapor Phase," T.R. Dyke, Topics in Current Chemistry, **120**, 86 (1984).

"The Microwave and Radiofrequency Spectrum of $\text{H}_2\text{S}\cdot\text{Ar}$," R. Viswanathan and T.R. Dyke, J. Chem. Phys. **82**, 1674 (1985).

"Coherent Raman Spectroscopy of HCN Complexes," G.A. Hopkins, M. Maroncelli, J.W. Nibler and T.R. Dyke, Chem. Phys. Lett. **114**, 97 (1985).

"Rotational Spectra and Structure of the Ammonia-Water Complex," P. Herbine and T.R. Dyke, J. Chem. Phys. **83**, 3768 (1985).

"Infrared and Coherent Raman Spectroscopy of HCN and DCN Dimers and Trimers," M. Maroncelli, G.A. Hopkins, J.W. Nibler, and T.R. Dyke, J. Chem. Phys. **83**, 2129 (1985).

"Molecular Beam, Infrared Absorption Studies of Rare Gas-OCS Complexes, G.D. Hayman, J. Hodge, B.J. Howard, J.S. Muentert, and T.R. Dyke, Chem. Phys. Lett. **118**, 12 (1985).

"CARS Spectra of van der Waals Complexes: The Structure of CO_2 Dimer," G.A. Pubanz, M.P. Maroncelli and J.W. Nibler, Chem. Phys. Lett. **120**, 313 (1985).

"Infrared Absorption Spectroscopy of $\text{Ar}\cdot\text{N}_2\text{O}$," G.D. Hayman, J. Hodge, B.J. Howard, and T.R. Dyke, Trans. Faraday Soc. In Press.

"Tunneling-Rotational Spectra for Water Dimer," J.A. Odutola, D. Prinslow, G. Johnson, and T.R. Dyke. In preparation.

"Rotational Spectra and Structure of the $\text{NH}_3\cdot\text{H}_2\text{S}$ Complex," P. Herbine, G. Johnson, A. Hu and T.R. Dyke. In preparation.

"Infrared Absorption and Microwave-Infrared Double Resonance Studies of $\text{Ne}\cdot\text{OCS}$ Molecular Beams," G.D. Hayman, J. Hodge, B.J. Howard, J.S. Muentert, and T.R. Dyke. In preparation.

Personnel:

University of Oregon

Thomas R. Dyke, Professor of Chemistry

Gary Johnson, Research Associate (Post-doctoral)

Peter Herbine, Research Assistant (Graduate Student)

PhD degree, 1985. Thesis: "Molecular-Beam Electric

Resonance Spectroscopy of Ammonia-Water and

Ammonia-Hydrogen Sulfide."

Albert Hu, Research Assistant (Graduate Student)

Oregon State University

Joseph W. Nibler, Professor of Chemistry

Shih-Yu Hou, Research Associate (Post-doctoral)

Mark Maroncelli, Research Associate (Post-doctoral)

Glenn Hopkins, Research Assistant (Graduate Student)

MS degree, 1984. Thesis: "Vibrational Spectroscopy
of Hydrogen Bonded Species."

George Pubanz, Research Assistant (Graduate Student)

PhD degree, 1986. Thesis: "Non-Linear Raman
Spectroscopy of Molecules in Supersonic Jets."

Recent Conference Presentations and Seminars Related to Project:

T.R. Dyke

AFOSR Molecular Dynamics and Surface Chemistry Conference,
Albuquerque, New Mexico, 10/25/84. Invited talk.

Faraday Division, Royal Society of Chemistry, High Resolution
Spectroscopy Group Conference, Reading, U.K., 12/17/84,
Contributed talk.

University of Bristol, Department of Theoretical Chemistry,
Bristol, U.K., 2/7/85. Invited seminar.

Oxford University, Physical Chemistry Laboratory, Oxford,
U.K., 2/11/85. Invited seminar.

University of Nottingham, Department of Chemistry,
Nottingham, U.K., 2/25/85. Invited seminar.

University of Sussex, School of Chemistry and Molecular
Sciences, Brighton, U.K., 2/28/85. Invited seminar.

Katholieke Universiteit, Physics Department, Nijmegen,
Netherlands, 4/2/85. Invited colloquium.

Xth International Symposium of Molecular Beams, Cannes,
France, 6/6/85. Contributed poster.

University of Colorado, Department of Chemistry and JILA,
5/16/86. Invited seminar.

American Physical Society DAMOP/DCP Meeting, Eugene, Oregon,
6/18/86. Contributed talk and poster.

J.W. Nibler

Western Spectroscopy Association Meeting, Asilomar,
California, 1/85. Contributed poster.

Sandia National Laboratory, Livermore, California, 3/85.
Invited seminar.

University of Puerto Rico, Department of Physics, San Juan,
Puerto Rico, 3/85. Invited Seminar.

International Laser Science Conference, Dallas, Texas,
11/85. Invited talk.

Western Spectroscopy Association Meeting, Asilomar,
California, 1/86. Contributed poster.

American Physical Society DAMOP/DCP Meeting, Eugene, Oregon,
6/18/86. Contributed poster.

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The objectives of this research project are to study the rotational and vibrational spectroscopy of hydrogen bonded complexes and van der Waals molecules and to develop new techniques for gathering this information. The long range purpose of this work is to provide basic information for modelling the effects of these molecules in atmospheric phenomena and to achieve insights concerning the intermolecular forces manifested in the weak bonds holding cluster molecules together. Rotational spectra were investigated with the molecular beam electric resonance method. High resolution radiofrequency and microwave spectra of complexes observed by this technique give accurate rotational constants, electric dipole moments, and nuclear hyperfine interaction data which was used to provide structural data. In this work the (H₂O)₂ molecule was found to have a-type transitions split by a tunneling doubling (continued on back)					
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of 19,527 MHz. Such tunneling splittings greatly complicate the rotation-vibration energy levels of water dimer and may thereby contribute to the "anomalous" atmospheric absorption problem. The spectra and structures for $\text{NH}_3 \cdot \text{H}_2\text{O}$ and $\text{NH}_3 \cdot \text{H}_2\text{S}$ were determined, each having a similar, linear hydrogen bonded configuration, and no evidence for proton transfer to the ammonia was observed. The $\text{N} \cdots \text{O}$ distance for the former complex was found to be the same as the $\text{O} \cdots \text{O}$ distance in water dimer, although the ammonia complex would be expected to have a stronger hydrogen bond. Structural data for the very weakly bound $\text{Ar} \cdot \text{H}_2\text{S}$ complex was obtained and the complex does not appear to be "hydrogen bonded".

Methods were developed for observing vibrational spectra of complexes in molecular beams using CARS. Raman spectra were obtained for molecular beams of HCN and DCN polymers in the CN and CH stretching regions. A force field model for the axial modes of these molecules was constructed by combining infrared and Raman data. Additionally, the infrared data supported a linear structure for HCN trimer. A similar study of CO_2 clusters in the symmetric stretching region demonstrated that the rule of mutual exclusion holds for $(\text{CO}_2)_2$, supporting a slipped parallel C_{2h} structure. In preliminary experiments, rotational CARS spectra of molecular beams of N_2 monomers were obtained with Raman shifts as low as a few cm^{-1} , illustrating that these methods can be extended to the low frequency intermolecular mode part of the vibrational spectrum.

In a collaborative project with B.J. Howard and J.S. Muentner, carried out at Oxford University, infrared absorption spectra for molecular beams of rare gas-OCS complexes in the ν_2 monomer mode region were obtained using tunable diode lasers. The spectra are rotationally resolved and the Doppler limited linewidths (0.004 cm^{-1}) show no evidence of vibrational predissociation broadening. Combination of the infrared absorption data and microwave-infrared double resonance experiments gave accurate rotational and centrifugal distortion parameters for these van der Waals molecules.

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