Polarity of van der Waals Molecules[1]

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Abstract: The polarity of a number of loosely bound complexes is qualitatively measured by molecular beam electric deflection. The following species are observed as polar: ArNO, ArHCl, NeDCl, XeHCl, $ArBF_3$, $KrBF_3$, $(NO)_2$, $(HCl)_2$, BF_3NO, BF_3CO, $(CO_2)_2$. Among the species observed to be nonpolar are: $(NO)_3$, $(NO)_4$, N_2O_2, NeHCl, COH_2, $(BF_3)_2$, $(BF_3)_3$, $(BF_3)_4$. Structural interpretations of these results, together with some preliminary radiofrequency spectroscopy, are presented.

It has been known for some time that molecular clusters, van der Waals complexes, are formed when a gas or mixture of gases is expanded through a supersonic nozzle.[2–5] During the expansion the internal degrees of freedom are cooled and many of the weakly bound complexes that are formed do not possess enough energy to dissociate. These species are of interest for several reasons. They are believed to be intermediates in termolecular reactions, for example, those involving nitric oxide.[6] The water dimer has been detected in the atmosphere.[7] Alkali metal dimers have been used in molecular beam reactive scattering experiments,[8] and molecular beams of dimers have been used to investigate the mechanisms of chemiluminescent gas reactions.[9,10]

The conditions under which polymers are formed during supersonic expansion have been extensively investigated using mass spectroscopy, and for argon dimer estimates have been made of the rate coefficient for dimer formation.[3] Water polymers up to $(H_2O)_{17}$ have been produced by supersonic expansion and the polarity of the lower mass polymers has been determined.[11] Dyke, *et al.*,[12] investigated the relaxation effects which occur during supersonic expansion by measuring radiofrequency line widths of one of the species in the beam (HCN) using an electric resonance spectrometer. It is well established that in addition to polymerization, effective rotational, translational, and vibrational relaxation occurs.

The structure of gas phase van der Waals complexes is relatively unexplored. Vacuum ultraviolet absorption by He_2, Ne_2, Ar_2, and Kr_2 in high-pressure gases has been observed and analyzed by Tanaka and coworkers.[13–15] The understanding of rare gas intermolecular potentials which are the subject of countless investigations has been greatly improved by recent crossed beam scattering experiments.[16] Diffuse ultraviolet absorption in nitric oxide has been attributed to the dimer[17] and a structure was proposed for $(NO)_2$ on the basis of infrared band shapes in gaseous nitric oxide absorption spectra.[18] However, the geometric accuracy is too low to permit comparing these gas phase results with the structure of $(NO)_2$ in the crystal.[19,20] Infrared spectra have also been reported for hydrogen-bonded clusters incorporating hydrogen fluoride.[21] Electron diffraction has recently been used to investigate very large molecular clusters (a few thousand molecules per cluster) resulting from supersonic expansion.[4] The infrared spectrum of gas phase $(CO_2)_2$ has been studied by Mannik, Stryland, and Welsh,[22] that of $(O_2)_2$ by Long and Ewing,[23] that of O_2–Ar by Henderson and Ewing,[24] and that of H_2–rare gas atom by Welsh and coworkers.[25–28] The microwave and radiofrequency spectra of hydrogen fluoride dimer have been analyzed by Dyke, *et al.*,[29] and its structure and dynamics well determined. More recently the rotational spectra and the structure of the ArHCl complex have been analyzed by Novick, *et al.*,[30] and the radiofrequency spectra of water dimer has been

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Table I. Electric Deflection Data for van der Waals Molecules

Source gas(es)	Temp, °K	Polymer	Ion	% refocusing[a]	Polarity
Atom–Atom					
Ar	147	Ar_2	Ar_2^+	Defocused	Nonpolar
		Ar_3	Ar_3^+	Defocused	Nonpolar
Kr	147	Kr_2	Kr_2^+		
Xe	147	Xe_2	Xe_2^+		
Atom–Diatomic					
Ar + NO	140	ArNO	$ArNO^+$	20	Polar
Ar + HCl	298	ArHCl	$ArHCl^+$	80	Polar
Ne + HCl	298	NeHCl	$NeHCl^+$	Defocused[b]	"Nonpolar"
Ne + DCl	298	NeDCl	$NeDCl^+$	5	Polar
Xe + HCl	298	XeHCl	$XeHCl^+$	50	Polar
Atom–Polyatomic					
Ar + BF_3	147	$ArBF_3$	$ArBF_2^+$	20	Polar
Kr + BF_3	147	$KrBF_3$	$KrBF_3^+$	3[c]	Polar
Diatomic–Diatomic					
NO	112	NO	NO^+	77	Polar
		$(NO)_2$	$(NO)_2^+$	6	Polar
		$(NO)_3$	$(NO)_3^+$	Defocused	Nonpolar
		$(NO)_4$	$(NO)_4^+$	Defocused	Nonpolar
$N_2 + O_2$	77	N_2O_2	$N_2O_2^+$	Defocused	Nonpolar
		$(N_2)_2$	$(N_2)_2^+$	Defocused	Nonpolar
		$(O_2)_2$	$(O_2)_2^+$	Defocused	Nonpolar
H_2 + CO	77	COH_2	COH_2^+	Defocused	"Nonpolar"
Cl_2	210	$(Cl_2)_2$	$(Cl_2)_2^+$		
HCl[d]		$(HCl)_2$	$(HCl)_2^+$	1	Polar
HF[e]		$(HF)_2$	H_2F^+	Refocused	Polar
Diatomic–Polyatomic					
NO + BF_3	147	BF_3NO	BF_2NO^+	6	Polar
CO + BF_3	147	BF_3CO	BF_2CO^+	6	Polar
Polyatomic–Polyatomic					
BF_3	183	$(BF_3)_2$	$B_2F_5^+$	Defocused	Nonpolar
		$(BF_3)_3$	$B_3F_8^+$	Defocused	Nonpolar
		$(BF_3)_4$	$B_4H_{11}^+$	Defocused	Nonpolar
CO_2	196	$(CO_2)_2$	$(CO_2)_2^+$	1	Polar
HCN	283	$(HCN)_2$	$(HCN)_2^+$	Refocused	Polar
NO_2[f]	298	$(NO_2)_2$	$(NO_2)_2^+$	Defocused	Nonpolar
		$(NO_2)_3$	$(NO_2)_3^+$	Defocused	Nonpolar
		$(NO_2)_4$	$(NO_2)_4^+$		
		$(NO_2)_5$	$(NO_2)_5^+$		
1,3-Butadiene	298	$(C_4H_6)(C_2H_4)$	$C_6H_{10}^+$	1	Polar
and ethylene[g]		$(C_2H_4)_2$	$C_4H_8^+$	Defocused	Nonpolar

[a] Whenever possible, the refocusing is given as a percentage of the straight through beam intensity when the maximum focusing voltage of 25 kV is applied to both focusing quadrupole fields. [b] For an explanation of this seemingly paradoxical behavior see the text. [c] The refocusing properties of $ArBF_3$ and $KrBF_3$ are more similar than this number implies. More experimental time was spent on the $ArBF_3$ system and its refocused intensity was optimized more carefully than that of $KrBF_3$. [d] See ref 11. [e] See ref 26. [f] See ref 34. [g] See ref 33 and 35.

analyzed by Dyke and Muenter.[31] Reference 32 is an experimentally oriented review article on van der Waals molecules which discusses some of these systems.

The present paper presents a semiquantitative survey of the polarity of a number of van der Waals complexes. The report is partially preliminary since detailed rotational spectroscopy is in progress on some of the species.

Experimental Section

Molecular beams of van der Waals molecules are produced by expanding the parent gas or gas mixture through a supersonic nozzle. The gas mixture is temperature controlled before expansion and usually the gases are cooled to as low a temperature as the vapor pressure requirements permit. With the relatively slow pumping speed of our system, it is necessary to use small diameter nozzles in order to maintain high reservoir pressures behind the nozzle.[33] Attempts were made to keep the channel length of the nozzle as short as possible. Other than this, no attempt at shaping the nozzle was made. No true skimmers are employed in this work. The first interchamber slit is typically a few thousand nozzle diameters from the nozzle. The gas therefore traversed the region from hydrodynamic to free molecular flow long before it reached this first slit.

The apparatus is a molecular beam electric resonance spectrometer. The state selecting and focusing fields are quadrupoles 34 cm long with a radius of 0.25 cm. Electrostatic potentials of up to 25 kV can be applied. The two quadrupole fields are separated by a resonance region (not used in the present work) 30 cm long. The overall distance from source to detector is 175 cm. A stop wire which shadows the gas source from the detector is inserted during focusing experiments.

The conditions for the focusing of molecules by a multipole electrostatic field have been discussed frequently.[34] Since the quadrupole structure has a minimum electric field at its center, it acts as a focusing lens for states with a positive Stark coefficient. A molecule is considered to be polar if it has thermally occupied levels with positive Stark coefficients (increasing energy in increasing elec-

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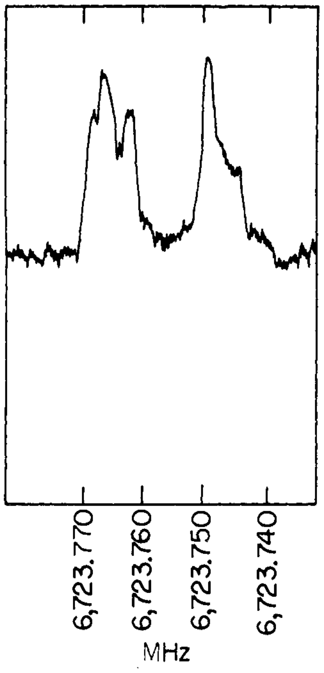

Figure 1. High-resolution microwave transition of ArHCl^{35}, $J = 2 \rightarrow 1$. The "structure" is due to interaction between the radiation field and the monovelocity beam and contains no molecular information.

tric field). For rigid molecules at a temperature high enough to populate several rotational levels, this operational definition of polarity is in complete accord with more conventional definitions of polarity. In the present work a supersonic nozzle is used as a gas source. Since the gas flow is hydrodynamic, all species have approximately the same velocity independent of their mass. This leads to somewhat different focusing behavior than is found with a thermal effusive source where the focusing for a given molecular species is a function of the source temperature only. In any system, the set of quantum states that has dipole matrix elements only with higher energy states will have negative Stark coefficients. Since rather dramatic cooling occurs upon supersonic expansion, interesting polarity behavior can result with the present gas source. If, however, the effective temperature is such that a reasonable proportion of states with positive Stark coefficients are populated, then in general for asymmetric top molecules with second-order moments, a dipole moment of 0.3 D or greater is required for unambiguous refocusing, while for rigid symmetric top molecules which possess first-order moments, a much smaller moment is required. (For example, CH_3D with a moment of 0.005 D has been refocused in this apparatus.[35])

Detection of the beam is performed by electron bombardment followed by mass analysis of the resultant ions. Several of the species studied contain fluorine, and for these species the parent ion peak in the mass spectrum is usually absent or of very low intensity. In these cases the polarity is determined by using lower mass fragment ions. The presence of two boron isotopes and two chlorine isotopes is useful in confirming the identity of particular ions in the mass spectrum.

It was found that high pressures and a small nozzle diameter were most effective in efficiently producing van der Waals molecules, especially in cases where the bonding might reasonably be expected to be weakest (Ne "compounds," for example). It was also found that cooling the gas or gas mixture increased the amount of complexes formed and so in general the gases were cooled to temperatures consistent with the required partial pressures desired behind the nozzle. When mixed complexes were required (for example, $ArBF_3$), the ratio of the constituent gases was also a critical factor, different ratios favoring the formation of different complexes (Ar_n, $ArBF_3$, and $(BF_3)_n$, for example).

Results and Discussion

The focusing behavior of the species studied is summarized in Table I which gives the focusing as a percentage of the beam intensity with the stop wire removed (straight through beam). Due to geometrical differences in some of the experimental conditions, the absolute numbers are not strictly comparable. Some of the experiments merit additional discussion.

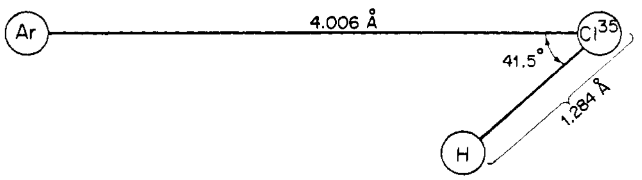

Figure 2. The structure of ArHCl. The angle of 41.5° represents the $\cos^2 \theta$ weighted average over the large amplitude zero-point angle bending motion.

$(Ar)_n$. Argon polymers up to $n = 3$ were observed at 147°K using a $30\text{-}\mu$ diameter nozzle and backing pressures greater than 1 atm. The relative intensity of the mass peaks at m/e 40, 80, and 120 were $1:7 \times 10^{-3}:5 \times 10^{-5}$, respectively. Ar_2 was also present in beams formed from mixtures of Ar and HCl, even from gases expanded from room-temperature reservoirs. Milne and Greene[36] have estimated the mole fraction of Ar_2 produced by expanding 1 atm of Ar through a $25\text{-}\mu$ nozzle to be 10^{-3}, and Golomb, Good, and Brown[3a] have been able to produce dimer mole fractions in excess of 0.5.

ArNO. An ion which can be assigned to the cluster ArNO appeared at m/e 70 when nitric oxide and argon were mixed in the ratio 1:6 at 147°K and expanded through the nozzle. Ions attributed to Ar_2 and $(NO)_2$ were also present; the relative abundances were $(Ar)_2^+:(NO)_2^+:ArNO^+ = 12:5:3$. The species ArNO refocused strongly.

ArHCl, NeHCl, NeDCl, and XeHCl. These species were produced under a variety of source temperatures, pressures, and gas mixtures. In order to minimize $(HCl)_2$, an excess of the rare gas is used and the source is not cooled below room temperature. The microwave spectrum and molecular structure of ArHCl has been determined.[30] A typical microwave spectrum of ArHCl is shown in Figure 1. The structure of the molecule is shown in Figure 2. The amplitude of oscillation of the hydrogen is large in the ground state. There is net orientation of the HCl with respect to the Ar–Cl axis. Thus, this molecule behaves as a normal polar molecule. XeHCl is polar implying also a net orientation of the HCl with respect to the Xe–Cl axis.

The species NeHCl and NeDCl show dramatically effects of nonrigidity. We note that while NeDCl is slightly polar, NeHCl appears nonpolar. Under the source conditions used, HCl is also nonpolar while DCl is slightly polar. For a diatomic molecule the lowest energy state with a positive Stark coefficient is $J = 1$, $M_J = 0$. For HCl, this state is at 21 cm^{-1} while for DCl it is at 10.8 cm^{-1}. The focusing data are taken to show that the rotational temperature of hydrogen chloride is about 10°K.

If NeHCl were similar to ArHCl with respect to the average orientation of the HCl along the Ar–Cl axis, NeHCl would appear polar, since the expected rotational constant is about 0.08 cm^{-1}. It seems likely

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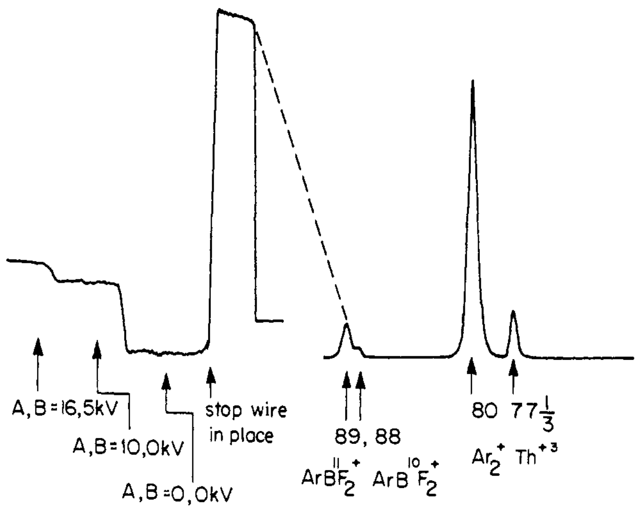

Figure 3. Mass spectrum of Ar + BF_3 in region *m/e* 75 to 90. Also shown is the refocusing behavior of $ArBF_3$ as monitored on the $ArB^{11}F_2$ ion peak.

that NeHCl consists of a free rotor HCl bound by a radial (with virtually no angular) potential to Ne. The first possible polar state of NeHCl would correspond to $J = 1$ HCl. It is likely from both considerations of the rotational temperature of HCl and the extensive negative search for higher states of ArHCl that the polar excited state of NeHCl is not populated under the present conditions. The polarity of NeDCl can be interpreted either as due to a *slight* average orientation of DCl along the Ne–Cl axis or population of the first excited state of NeDCl. The nature of the bonding in NeDCl will be answered by microwave spectroscopy.

The differences in the angular potential of inert gas–HCl species appears to us to be considerably more dramatic than likely differences in bond lengths or strengths.

$ArBF_3$. Figure 3 shows the mass spectrum of Ar + BF_3 and the typical refocusing behavior of $ArBF_3$ indicating that it is a polar species. The gas source is 10% BF_3 and 90% Ar. Figure 4 shows two radiofrequency resonances. A number of radiofrequency resonances have been observed. The resonance frequency varies linearly with electric field indicating that $ArBF_3$ is most likely a symmetric top. This places the argon on the three-fold axis of symmetry. The spectroscopic study is not complete. It appears likely that the electric dipole moment of $ArBF_3$ is approximately 0.2 D. Such a large moment is most likely due to a distortion of the BF_3 submolecule rather than to charge transfer. This speculation will be tested by future spectroscopy.

$(NO)_n$. Nitric oxide polymers up to $(NO)_4$ were detected using the smallest diameter nozzles and reservoir pressures up to 2 atm. The relative magnitudes of the ion peaks at *m/e* 30, 60, 90, and 120 were $1:1 \times 10^{-2}:5 \times 10^{-4}:6 \times 10^{-5}$. The trimer and tetramer defocused while the dimer refocused. Preliminary spectroscopy has been undertaken on $(NO)_2$ in this laboratory.[37,38]

N_2O_2. The van der Waals complex N_2O_2 formed by expanding a mixture of N_2 and O_2 through the nozzle is, of course, an entirely different species from the $(NO)_2$ formed from nitric oxide expansion. N_2O_2 is nonpolar while $(NO)_2$ is polar. These two species are "van der Waals isomers" of each other.

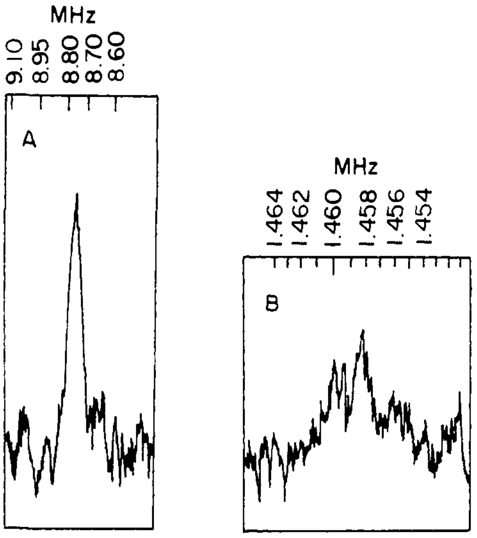

Figure 4. Radiofrequency resonances of $ArB^{11}F_3$. (a) A resonance obtained under low resolution conditions. Stark field = 984 V/cm. (b) A resonance obtained under conditions of high resolution. Stark field = 98.4 V/cm.

COH_2. This species is the van der Waals isomer of formaldehyde. It appears as a nonpolar species in our apparatus. The complex almost certainly has a dipole moment near 0.1 D; however, the velocity of the beam is high due to the H_2; thus, it is not refocusable.

$(HCl)_2$. The dimer of hydrogen chloride in a molecular beam has been previously observed by Dyke, *et al.*,[12] and we confirm that it is a polar species. It would appear likely that the structure of $(HCl)_2$ is similar to that of $(HF)_2$[29] and that this molecule also will show the peculiar inversion motion breaking and reforming its hydrogen bond. Conformation of this will have to await spectroscopic investigation.

$(CO_2)_2$. Our observation that the dimer of nonpolar carbon dioxide is a polar species is consistent with the T-shaped form for the complex proposed by Mannik, *et al.*[22] If the CO_2 submolecule that forms the top of the T is slightly distorted, a small dipole moment would be expected.

$(NO_2)_n$. These molecules are discussed in ref 39.

(1,3-Butadiene)(ethylene). This polar, perhaps "pre-Diels–Alder," complex is discussed in ref 38 and 40.

The catalog of molecules presented in this paper is by no means an exhaustive list of the types and varieties of van der Waals molecules that can readily be produced by supersonic expansion and studied in a molecular beam. It is likely that virtually any complex can be produced in this manner.

The structural information available from analysis of the molecular beam spectra of $(HF)_2$,[29] ArHCl,[30] and $(H_2O)_2$[31] illustrates the detail that can be obtained for van der Waals and hydrogen-bonded complexes using supersonic expansion to form the molecules for study by high-resolution molecular beam spectroscopy.

Acknowledgment. The authors acknowledge the help of Stephen Harris on the rare gas–HCl experiments.

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