VIBRATIONAL ENERGY DISTRIBUTION IN BaI PRODUCED IN REACTIONS OF VAN DER WAALS MOLECULES

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The reactions of Ba with CF3I dimers and CH3IAr complexes were studied applying the laser induced fluorescence (LIF) technique. It was found that the BaI produced from the dimers contains about 20 kcal/mole less vibrational energy than the BaI produced in the corresponding monomeric reaction. The CH3IAr on the other hand, yielded only a slightly colder vibrational distribution than the monomers.

1. INTRODUCTION

Van der Waals (vdw) molecules and clusters provide a medium for the study of intermolecular forces as well as the transition from the isolated molecule to the condensed phase. Vdw molecules as partners in reactions, can introduce several effects that are not found among isolated molecules. For example a dynamic effect is expected due to the existence of very low frequency modes, which correlate to the intermolecular bonds, in the vdw complex. Therefore the excess energy in the collision complex would be deposited mainly in rotation and translation rather than in vibrations. In addition, because of the increase in the density of states in the collision complex, its lifetime may be lengthened.
In several reactive scattering experiments (1,2), and in recent experiments done in our laboratory (3,4), it has been shown that information obtained by cross beam experiments, in which only two species collide, cannot be simply extrapolated to the condensed phase, and that even a single "spectator" which is involved in the process can effectively induced different types of phenomena. Recently "photochemistry" experiments of vdw complexes (5,6) yielded interesting results on reaction mechanisms and orientation effects.

In this work two reactions will be discussed:

\[(\text{CF}_3\text{I})_2 + \text{Ba} \rightarrow \text{BaI}+ \ldots. \tag{1}\]

\[\text{CH}_3\text{IAr}+\text{Ba} \rightarrow \text{BaI}+ \ldots. \tag{2}\]

These systems were chosen because the mechanisms of the monomeric reactions were studied, applying laser induced fluorescence (LIF) (7,8) and reactive scattering techniques (9), and the products were found to include large amounts of the excess energy in the form of vibrational motion. Hence the effect of a "third body" attached to the reactants may manifest itself as a dramatic change in the way energy is disposed among the different degrees of freedom.

2. EXPERIMENTAL

The experiment was carried out applying a crossed beam arrangement (Figure 1). The vacuum system consisted of two chambers, each pumped by a 6" diffusion pump. One chamber served as the source of the molecular beam, with a 1 ms pulsed nozzle (fuel injector from Bosch) with a hole diameter of 0.2 mm. A quadrupole field, consisting of
6 mm diameter and 19 cm long stainless steel rods, was used to separate the CF$_3$I monomers, which have a large dipole moment, from the dimers which are barely polar. The rods are insulated from each other by being mounted on the inside of a pair of sapphire rings, so that the internal diameter of the quadrupole system is 3 mm. Two opposing rods were connected to ground; while the other two to a high voltage power supply. In between the rods a teflon stop wire was placed (10), so that as it was turned to one side it blocked the central part of the path inside the quadrupole. Because the teflon stop had a hole in the center, when it was positioned perpendicular to the beam, only species that are not focused could pass. A voltage of 15KV was needed to observe the focused CF$_3$I monomers. A collimator with a 5 mm hole was placed between the source chamber and the reaction chamber, so that background molecules contributed very little to the observed signal.

The Ba atomic beam was introduced perpendicular to the molecular and laser beams. It was produced from an
oven as described in ref. (4). The typical operating temperature was 1090 K. The excitation spectrum of the products was obtained with a flashlamp pumped dye laser (Chromatix CMX-4) with fwhm of 4 cm\(^{-1}\). An EAI 250 mass spectrometer was used to ascertain the existence of clusters in the beam. However no quantitative conclusions could be reached because of the extensive fragmentation occurring in the ionizer.

3. RESULTS AND DISCUSSION

In Figure 2 the LIF spectra of BaI is presented.

![Figure 2](image)

**FIGURE 2** LIF spectra of BaI produced by the (a) monomeric reaction Ba+CF\(_3\)I, or by the (b) dimeric reaction Ba+(CF\(_3\)I\(_2\)).

Curve (a) is obtained as monomers of CF\(_3\)I react, while curve (b) is seen as most of the monomers are deflected, and the beam contained mainly dimers. As it is well known the monomers produce BaI with a vibrational distribution.
that peaks at $v"=50$ (7). In contrast the dimers produce a vibrational distribution that peaks at $v"=10$. Some remaining monomers in the beam contribute to a small extent to curve b, as seen by the small "monomeric" peak also present. This change in the distribution corresponds to a decrease of about 20 kcal/mole in the vibrational energy, which can not be attributed to the change in exothermicity of the reaction due to the vdw bond.

Munakata and Kasuya have studied the reaction of Ba with CF$_3$Br (11). They found that when the CF$_3$Br was seeded in He a bimodal distribution of the vibrational energy was observed. For high He pressure the vibrational energy peaked at about $v"=12$ instead of $v"=30$ for the pure CF$_3$Br. Although they attributed their result to the change in collision energy, its similarity to our observations suggests the possibility that dimers of CF$_3$Br may be responsible for this effect. It is important to note that no change in translational energy was involved in our study, and only neat CF$_3$I was used.

In Figure 3 the LIF spectra of BaI produced by the reaction of Ba with a CH$_3$I is shown. Curve a corresponds to a beam containing neat 400 torr CH$_3$I, while curves b and c were produced with beams containing 1:40 and 1:80 CH$_3$I:Ar, respectively. The total stagnation pressure was 1200 torr. In these two cases the beams contained CH$_3$IAr clusters as was monitored by the mass-spectrometer. The amount of CH$_3$IAr complexes in the beam increased with increasing Ar concentration. As seen from the figure the amount of vibrational energy in the product BaI changed only slightly and its peaks at $v"=16$ for the vdw complex compared to $v"=20$ for the monomer.
FIGURE 3 LIF spectrum of BaI produced by the reaction of (a) Ba+CH₃I and (b), (c) Ba CH₃I Ar. Note that the relative contribution of the monomeric reaction decreases with increasing Ar concentration (see text).

The different effects in the two reactions may be explained by the vdw bond strength and by the structure of the complex. In the reaction of (CF₃I)₂, the dimeric bond contributes six additional degrees of freedom to the reaction complex. Because of their very low frequencies, they behave like phonons in the condensed phase. Therefore, they contribute greatly to the density of states in the reaction complex, and a significant portion of the energy is deposited in them. Since these modes correspond to translational or rotational motion, once the dimer dissociates much less energy remains in the vibration of the BaI. In the reaction of CH₃I Ar the vdw bond strength is weaker, and the number of additional degrees of freedom due to the existence of the spectator is smaller too. In addition,
the Ar atom is, most probably, closed to the I atom side, and therefore in order for the reaction to occur the Ar atom has to be removed. We conclude therefore that the small change in the vibrational energy in the product in reaction 2 is due to fast dissociation of the collision complex, actually before the reaction ends.

Recently Chakravorty and Bernstein (12) studied the effect of long alkyl chains on the vibrational energy in the product BaI, resulting from the reaction of RCH\textsubscript{3}I (R=alkyl chain) with Ba. They found more vibrational energy as R became longer. This can be explained by the weakening of the C-I bond with increasing chain length. The long tail did not affect the energy distribution in the collision complex, probably due to the high localization of the process, which resulted in short lived collision complexes. The difference between this finding and those presented in this work are quite striking. In the vdw case ((CF\textsubscript{3}I)\textsubscript{2}) due to the head to tail shape of the complex, and the relatively efficient coupling between the two molecules, the excess energy can be distributed among all the degrees of freedom, and a "solvent" effect is present even for a single third body.

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REFERENCES