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

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The reactions of Ba with CF_3I dimers and CH_3IAr
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 pro-
duced in the corresponding monomeric reaction. The
CH_3IAr 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 me-

dium 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 intro-

duce 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 corre-

late 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 exper-
iments, 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 effect-
ively 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:

$(CF_3I)_2 + Ba \rightarrow BaI + \dots$ (1)

$CH_3IAr + Ba \rightarrow BaI + \dots$ (2)

These systems were chosen because the mechanisms of
the monomeric reactions were studied, applying laser induc-
ed fluorescence (LIF) (7,8) and reactive scattering tech-
niques (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
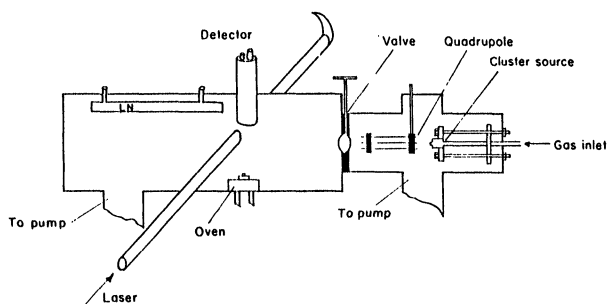diameter of 0.2 mm. A quadrupole field, consisting of

FIGURE 1   The experimental set-up

6 mm diameter and 19 cm long stainless steel rods, was
used to separate the CF_3I monomers, which have a large di-
pole 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_3I monomers.
A collimator with a 5 mm hole was placed between the source
chamber and the reaction chamber, so that background mole-
cules 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 tem-
perature was 1090 K. The excitation spectrum of the pro-
ducts was obtained with a flashlamp pumped dye laser (Chro-
matix CMX-4) with fwhm of 4cm^{-1}. An EAI 250 mass spec-
trometer 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

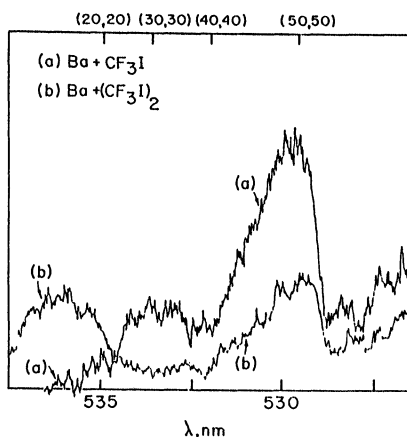In Figure 2 the LIF spectra of BaI is presented.

FIGURE 2   LIF spectra of BaI produced by the (a) mono-
            meric 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 re-
maining 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_3Br (11). They found that when the CF_3Br 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_3Br.
Although they attributed their result to the change in
collision energy, its similarity to our observations
suggests the possibility that dimers of CF_3Br may be res-
ponsible for this effect. It is important to note that no
change in translational energy was involved in our study,
and only neat CF_3I was used.

In Figure 3 the LIF spectra of BaI produced by the
reaction of Ba with a CH_3I is shown. Curve a corresponds
to a beam containing neat 400 torr CH_3I, while curves b
and c were produced with beams containing 1:40 and 1:80
CH_3I:Ar, respectively. The total stagnation pressure was
1200 torr. In these two cases the beams contained CH_3IArn
clusters as was monitored by the mass-spectrometer. The
amount of CH_3IAr 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.

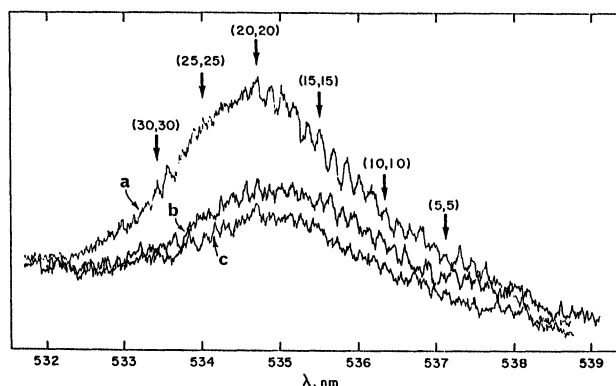FIGURE 3   LIF spectrum of BaI produced by the reaction of
            (a) Ba+CH$_3$I and (b), (c) Ba CH$_3$IAr. Note that
            the relative contribution of the monomeric
            reaction decreases with increasing Ar concen-
            tration (see text).

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 (CF$_3$I)$_2$, the dimeric bond
contributes six additional degrees of freedom to the reac-
tion 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 disso-
ciates much less energy remains in the vibration of the BaI.
In the reaction of CH$_3$IAr 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_3I
(R=alkyl chain) with Ba. They found more vibrational ener-
gy as R became longer. This can be explained by the weak-
ening 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 $((CF_3I)_2)$ 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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