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A velocity map ion imaging study of difluorobenzene-water complexes: Binding energies and recoil distributions

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The binding energies of the p-, m-, and o-difluorobenzene-H_2O complexes have been measured by velocity map ion imaging to be 922 ± 10, 945 ± 10, and 891 ± 4 cm^{-1}, respectively. The lack of variation provides circumstantial evidence for water binding to the three isomers via the same interaction, viz. an in-plane O–H$\cdots$F hydrogen bond to one of the fluorine atoms on the ring, with a second, weaker interaction of the water O atom with an *ortho* hydrogen, as determined previously for the p-difluorobenzene-H_2O complex [Kang *et al.*, J. Phys. Chem. A **109**, 767 (2005)]. The ground state binding energies for the difluorobenzene-H_2O complexes are $\sim 5\% - 11\%$ larger than that for benzene-H_2O, where binding occurs to the π electrons out-of-plane. However, in the S_1 state the binding energies of the o- and p-difluorobenzene-H_2O complexes are smaller than the benzene-H_2O value, raising an interesting question about whether the geometry at the global energy minimum remains in-plane in the excited electronic states of these two complexes. Recoil energy distributions for dissociation of p-difluorobenzene-H_2O have been measured from the $\overline{3^1}$, $\overline{5^2}$, and $\overline{3^1 5^1}$ levels of the excited electronic state. These levels are 490, 880, and 1304 cm^{-1}, respectively, above the dissociation threshold. Within the experimental uncertainty, the recoil energy distributions are the same for dissociation from these three states, with average recoil energies of ~ 100 cm^{-1}. These recoil energies are 60% larger than was observed for the dissociation of p-difluorobenzene-Ar, which is a substantially smaller increase than the 400% seen in a comparable study of dissociation within the triplet state for pyrazine-Ar, -H_2O complexes. The majority of the available energy is partitioned into vibration and rotation of the fragments. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2896081]

I. INTRODUCTION

The study of molecular complexes and clusters in the gas phase provides an important link with condensed phase behavior, with clusters considered as models for reagent surrounded by a specific number of solvent molecules.[1] Complexes involving water are of significance, with particular interest in water complexed to an aromatic molecule because of the relevance to biological processes.[2] Benzene-water complexes have been extensively studied experimentally and theoretically to determine the nature of the interaction as a model for hydrophobic interactions, as discussed in several reviews.[3–5] The binding energy and geometry of the benzene-water dimer have been determined.[3,5] A weak π-hydrogen bond is formed between the aromatic π electrons and one of the hydrogen atoms on the water molecule. The water molecule is located above the aromatic ring with both O–H bonds pointing toward the ring.

Substituents on the ring can significantly alter the aromatic-water interaction. Fluorine's influence on the aromaticity of the ring has recently been explored in detail.[6] There is a net destabilizing of the aromatic benzene system by the addition of fluorine, although π back bonding increases the electron density in the ring. In the case of

p-difluorobenzene (pDFB) complexes, it has been established experimentally that the water molecule does not interact with the π cloud. Instead, it forms an in-plane O–H$\cdots$F hydrogen bond to one of the fluorine atoms on the ring, with a second, weaker interaction of the water O atom with one of the two *ortho* hydrogens.[7] This is consistent with earlier calculations.[8,9] The remaining H atom appears to lie out of the plane. This change in the nature of the aromatic-water interaction has led us to explore the complexes of water with the series of difluorobenzenes (DFBs), *viz. para-*, *meta-*, and *ortho-*. The *meta-* and *ortho-*DFB-water complexes have been probed previously using resonance enhanced multiphoton ionization (REMPI).[10] A rotational contour analysis of the origin bands suggests that the complexes involve an in-plane O–H$\cdots$F hydrogen bond analogous to that seen in pDFB-water.[10]

The aim of our study is twofold. The first is to determine the binding energies of water to the DFBs and hence provide data on the strength of the water-difluorinated benzene interaction and on the extent to which the change in the relative positions of the fluorine atoms, which alters the aromaticity,[6] affects the strength of the interaction. The second is to explore the dissociation dynamics of the van der Waals complex, specifically the partitioning of energy into translation. This latter study is focused on the pDFB-water complex as there are data for the pDFB-Ar complex for comparison.[11]

For pDFB-Ar dissociation we found that (a) the translational energy release is low (average recoil energy ~ 63 cm^{-1}), (b) there is significant angular momentum in the pDFB fragment, and (c) the recoil energy distribution is insensitive to the initial vibrational energy and destination state density up to ~ 3000 cm^{-1} available energy. Yoder and Barker found in studies of dissociation of aromatic complexes from triplet states that H-bonded complexes released significantly more energy in translation than those involving dispersion interactions.[12] We here explore whether this trend is seen for the S_1 pDFB-H$_2$O versus pDFB-Ar complexes.

These issues will be explored using the technique of velocity map ion imaging.[13] This technique is ideal for studies of van der Waals molecule dissociation where the translational energy released is small (typically $\ll 1000$ cm^{-1}) because the image resolution is linear in velocity, and so the energy resolution is highest at low translational energies.

A number of studies of the pDFB-H$_2$O complex have been reported,[7–9,14,15] however, studies of the *ortho* and *meta* isomers appear restricted to a Ph.D thesis.[10] The $S_1 \leftarrow S_0$ transition of the pDFB-H$_2$O complex has been studied using both one and two-color $1+1$ REMPI.[8,14] The pDFB-H$_2$O origin transition is 169 cm^{-1} higher in energy than the pDFB monomer origin: The complex is more weakly bound in the excited electronic state. Similar blueshifts were reported for the other vibronic bands: $\overline{6_0^1}$ ($+169$ cm^{-1}), $\overline{8_0^2}$ ($+176$ cm^{-1}), and $\overline{5_0^1}$ ($+158$ cm^{-1}). The lack of progressions in the intermolecular modes suggested that the complex has similar geometries in the ground and excited electronic states. The geometry was explored in detail in a rotationally resolved study of the $S_1 \leftarrow S_0$ spectrum by Kang *et al.*[7] They found a tunneling splitting of bands in the spectrum, showing that the attached water undergoes a combined inversion-internal rotation motion. The H-bonding interaction has also been explored through the O–H stretch in the infrared.[15] The ionization potential of pDFB-H$_2$O was determined using two color $1+1'$ REMPI to be $72\,450 \pm 50$ cm^{-1},[14] although Brenner *et al.* note that as their calculations suggest a significant difference in geometry between the neutral and ionic states, the measured ionization threshold may be higher than the adiabatic ionization potential.[8]

The $S_1 \leftarrow S_0$ transitions of the mDFB-H$_2$O and oDFB-H$_2$O complex have been studied using mass resolved REMPI.[10] The mDFB-H$_2$O origin transition is 92 cm^{-1} blueshifted from the mDFB monomer, while the oDFB-H$_2$O origin transition is 105 cm^{-1} blueshifted from the oDFB monomer. Thus, like pDFB-H$_2$O, both complexes are more weakly bound in the excited electronic state, although the change in bond strength on electronic excitation is reduced in these two isomers.

II. EXPERIMENTAL DETAILS

The experimental details for the velocity map imaging experiments have been given previously.[16] Complexes are formed in a supersonic free jet expansion of the DFB (1%) and water (1%) in Ar at 6 atm backing pressure. Complexes are excited in the extraction region of a time of flight mass

TABLE I. Observed transitions for pDFB-H$_2$O.

Transition	Wavenumber (cm^{-1})	Shift from pDFB band (cm^{-1})[a]	Note
$\overline{8_0^2}$	37 359	163	b,c
	37 376	180	
$\overline{27_0^2}$	37 812	168	
$\overline{5_0^1}$	37 824	168	
$\overline{6_0^2}$	37 828	170	
$\overline{3_0^1}$	38 250	161	c
	38 255	166	
$\overline{5_0^2}$	38 638	164	
$\overline{5_0^1 6_0^2}$	38 640	164	
$\overline{3_0^1 5_0^1}$	39 065	158	c
	39 069	162	

[a]The pDFB-H$_2$O 0_0^0 band is 169 cm^{-1} higher in energy than that for pDFB (Refs. 8 and 14).
[b]Broad bands with unresolved substructure.
[c]Probable Fermi resonance.

spectrometer (ToFMS) operating in velocity map imaging mode[13] using the frequency doubled output of a Nd:YAG pumped dye laser (pulse duration of about 4 ns; frequency doubled line width of about 0.4 cm^{-1}). As is discussed in the following sections, the complexes dissociate within the S_1 state, producing S_1 DFB products that can absorb a second photon and be ionized. The ions are accelerated down the ToFMS and detected using a gated microchannel plate/phosphor screen combination with a charge coupled device camera. Images are downloaded shot-by-shot and analyzed by a laboratory computer to accumulate a histogram of ion count versus position. The images are isotropic, indicating that dissociation is slow compared with molecular rotation, and are reduced to plots of intensity versus radius (so-called radial plots) for analysis. Conversion of the radial plots to the original three-dimensional distribution is undertaken using the inverse Abel function method and the total energy distribution determined as described in Ref. 16. Ion images were calibrated using photoelectron images. The laser power was maintained such that only one to two ions were observed with each laser shot to eliminate Coulomb repulsion effects.

Spectra were obtained using the method of velocity and mass resolved REMPI.[17] Here, the center of each image and a surrounding annulus are integrated separately. DFB ions originating from dissociation of the complex gain kinetic energy and contribute intensity away from the center of the image, i.e., in the annulus. Table I summarizes the transition frequencies measured for pDFB-H$_2$O in key regions. The blueshift is reduced at higher vibrational energies.

Samples of pDFB and mDFB with water were stable; however, we found that, for samples of oDFB with water, the signal from the complex degraded over time. In this case fresh samples were made daily.

III. RESULTS

A. DFB-water binding energies

The binding energies for the DFB-H_2O complexes are determined using the technique of velocity map imaging discussed in Ref. 18. In essence, the complex is excited to a vibrational level not far above the S_1 dissociation energy and the translational energy distribution of the products measured. Because of the limited energy available to the products, the translational energy distribution is truncated. The binding energy is determined from the maximum translational energy released.

One of the keys to performing the experiment is determining an appropriate vibronic transition of the complex. In the absence of an accurate ionization energy for the complex, which would allow measurement of dissociation in the ion with the values for the neutral subsequently calculated, one requires rapid dissociation on the S_1 surface to prevent the complication of ionization of intact complexes and their subsequent dissociation. A second requirement is that the vibrational level excited must be sufficiently close to dissociation that the energy at which the recoil energy truncates is readily identified.

For pDFB-H_2O, limits for the binding energy have been determined experimentally.[8,14] An upper limit of 818 cm^{-1} was set by the appearance of fragment ions following 5_0^1 excitation. The energy of two photons at this wavelength is well above the pDFB-H_2O ionization potential so that fragmentation could occur from both excited and ionic states; however, a two-color $1+1'$ REMPI experiment established that the dissociation observed in the one-color experiment occurs from 5^1 in S_1. The lack of dissociation products following 6_0^1 excitation implied a lower limit of 410 cm^{-1} for S_1 dissociation. However, this was refined upwards as the failure of the ion to decompose after $1+1$ REMPI via 6_0^1 suggests a lower limit of 2334 cm^{-1} for the ion. Combined with the spectral shift for ionization, this gave a lower bound of 794 cm^{-1} in S_1. As we discuss later, this lower limit is less definite than the upper bound.

Figure 1 shows the recoil energy distribution for the products produced following excitation of $\overline{5}^1$ in pDFB-H_2O. The distribution is truncated because the translational energy available to the fragments in the dissociation process is limited. The cutoff is not as sharp as seen for pDFB-Ar,-Kr complexes,[19] presumably because some excess energy is partitioned into rotational motion of the H_2O fragment. To determine the position of the cutoff, we fit the signal and background components to quadratic functions. (The background comes from multiphoton ionization of pDFB remaining in the chamber between laser shots.) The intersection of these two curves (the solid lines in the figure) gives the maximum translational energy in the products, which in this case is 65 ± 10 cm^{-1}. From this value and the vibrational energy of $\overline{5}^1$, the binding energy in the excited state is calculated to be 753 ± 10 cm^{-1}. Binding energies for the remaining states are calculated from the shift in ionization potential [1421 ± 50 cm^{-1} (Ref. 14)] and the 169 cm^{-1} $S_1 \leftarrow S_0$ complex shift. They are summarized in Table II.

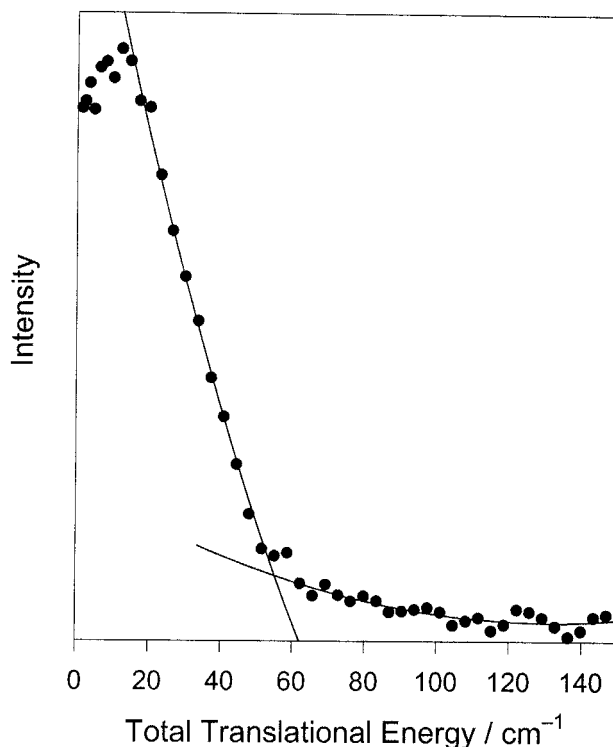In the case of mDFB-H_2O, Springfield noted a loss of

FIG. 1. The recoil energy distribution following dissociation of pDFB-H_2O from the $\overline{5}^1$ level ($\overline{0_0^0}+817$ cm^{-1}). The points are the experimental data while the solid curves are a fit to the signal and background regions of the distribution (see text).

features above $\overline{0_0^0}+931$ cm^{-1} at the parent mass in the REMPI spectrum, indicating rapid dissociation.[10] The $\overline{0_0^0}$ $+931$ cm^{-1} feature itself is also significantly diminished relative to the corresponding feature in the mDFB spectrum. These observations, coupled with the pDFB-H_2O dissociation energy, strongly suggest that dissociation occurs within S_1 at 931 cm^{-1}. An image taken at the mDFB mass with excitation on the $\overline{0_0^0}+931$ cm^{-1} band of mDFB-H_2O reveals the truncation characteristic of excitation just above the dissociation onset. Following the approach outlined above for pDFB complex, we determine a maximum excess energy of 78 ± 10 cm^{-1}. The corresponding binding energies are given in Table II.

For oDFB-H_2O, Springfield found a reduction in intensity at the parent mass in the REMPI spectrum above a

TABLE II. Experimentally determined binding energies for the DFB$-H_2O$ complexes.

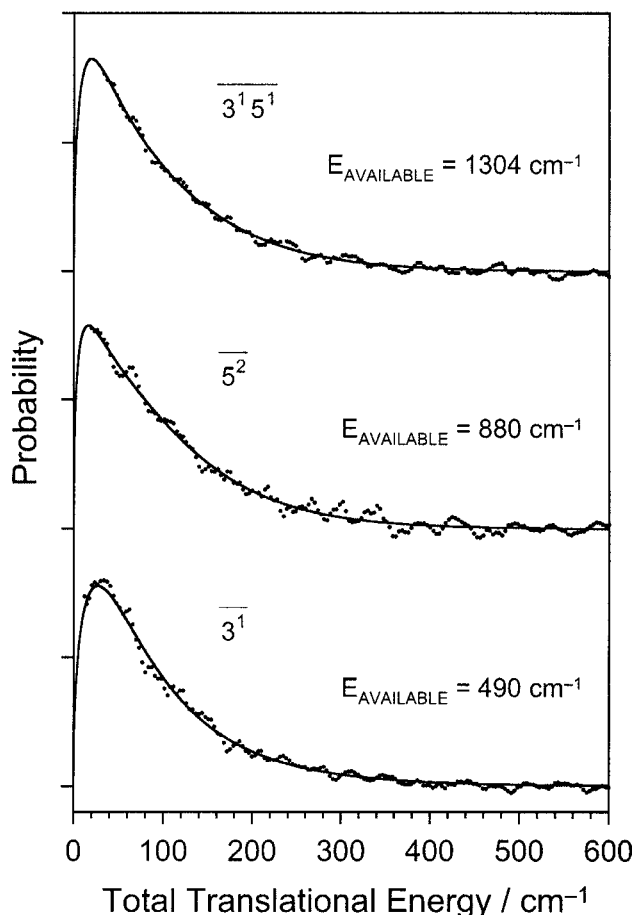|		Dissociation energy (cm^{-1})	
Isomer	Electronic state	This work	Martrenchard *et al.*
para	S_0 (D_0^0)	927 ± 10	$963 < D_0^0 < 987$
	S_1 (D_0^1)	758 ± 10	$794 < D_0^1 < 818$
	D_0 (D_0^+)	2348 ± 51	$2334 < D_0^+ < 2458$
meta	S_0 (D_0^0)	945 ± 10	
	S_1 (D_0^1)	853 ± 10	
ortho	S_0 (D_0^0)	891 ± 4	
	S_1 (D_0^1)	786 ± 4	

FIG. 2. Recoil distributions for dissociation of pDFB-H_2O from three S_1 vibrational levels.

strong band at $\overline{0_0^0}+722$ cm^{-1}, suggesting the onset of dissociation above this energy.[10] Through the use of velocity and mass resolved REMPI,[17] we identified a weak feature at 0_0^0 +823 cm^{-1} as the first band from which dissociation was detected. The truncated distribution gave a maximum excess energy of 37 ± 4 cm^{-1}; the corresponding binding energies are given in Table II.

B. Recoil energy distributions

Images have been obtained following dissociation from $\overline{3^1}$ ($E_{vib}=1243$ cm^{-1}), $\overline{5^2}$ ($E_{vib}=1633$ cm^{-1}), and $\overline{3^1 5^1}$ ($E_{vib} \sim 2057$ cm^{-1}) of pDFB-H_2O. The 3_0^1 and $3_0^1 5_0^1$ transitions appear as doublets (separation of 4–5 cm^{-1}); images were obtained from the higher energy, more intense of the pair. The signal was insufficient to obtain images of satisfactory quality for the higher energy $\overline{3^2 5^1}$ level. Since excitation of 5^1 leads to dissociation within S_1,[14] it is reasonable to deduce that at the higher vibrational levels investigated dissociation also occurs in S_1. The recoil energy distributions obtained from the images are shown in Fig. 2. The points represent the inverse Abel transformed data and the solid line is the fit by a function of the form

$$P(E) = \sqrt{E}\sum_{i=1}^{2} A_i e^{-k_i E}, \qquad (1)$$

which is equivalent to the sum of two Maxwell–Boltzmann distributions. The parameters for the fits to the distributions

TABLE III. A_i and k_i values for the fits [Eq. (1)] to the experimental recoil energy distributions for pDFB-H_2O.

Transition	A_1	k_1	A_2	k_2
3_0^1	0.001 73	0.0228	0.000 767	0.0115
5_0^2	0.001 82	0.0651	0.001 66	0.0139
$3_0^1 5_0^1$	0.001 51	0.0136	0.001 70	0.0450

are given in Table III. As we have observed previously,[11,16] this functional form provides an excellent fit to the data.

The three recoil distributions are very similar. They quickly rise to a maximum at 15–25 cm^{-1}, following which they decay in an exponential-like fashion to zero by $\sim$450 cm^{-1}. The average kinetic energy released to the fragments from each energy level investigated is given in Table IV. As we have found for the pDFB-Ar, pDFB$^+$-Ar, and benzene$^+$-Ar complexes,[11,16,20] most of the energy remains as internal energy of the fragments. There is essentially no change in the average kinetic energy released with increasing available energy.

IV. DISCUSSION

A. DFB-water binding energies

The S_0 binding energies for the three difluorobenzene isomers with water are very similar, lying in the range of 919 cm$^{-1}\pm3\%$. It has been established in pDFB-H_2O that water forms an in-plane O–H$\cdots$F hydrogen bond to one of the fluorine atoms on the ring, with a weaker interaction of the water O atom with an *ortho* hydrogen.[7] The lack of variation in binding energies is circumstantial evidence for water binding to the three. DFB isomers via the same interaction although, as we discuss below, the interaction is not significantly stronger than that seen for the out-of-plane interaction with the π electrons in benzene-H_2O. An in-plane structure for pDFB-H_2O and pDFB-H_2O is consistent with the rotational analysis of Springfield.[10] The experimental data does not allow us to comment on the possible existence of a second F$\cdots$H–O bond in the *ortho* and *meta* in-plane complexes.

Interestingly, the variation between isomers doubles, and their ordering changes, in the S_1 state. oDFB has the weakest bond in S_0, while pDFB has the weakest interaction in S_1. The binding is largest for mDFB in both states. This is presumably a result of the change in electron density in the excited electronic states of the different isomers. The lack of

TABLE IV. Values for the average translational energy released during the dissociation of pDFB-H_2O.

Initial Level	S_1 Vibrational Energy (cm^{-1})	Excess Energy (cm^{-1})	Average recoil Energy (cm^{-1})
$\overline{3^1}$	1243	490	101
$\overline{5^2}$	1633	880	100
$\overline{3^1 5^1}$	2057	1304	97

TABLE V. Calculated binding energies for pDFB–H_2O from Ref. 9. The σ and σ' structures are both "in plane," differing only in the precise position of the O atom with respect to the pDFB plane.

Level of theory and basis set	E_0 for σ geometry		E_0 for σ' geometry	
	kcal mol^{-1}	cm^{-1}	kcal mol^{-1}	cm^{-1}
MP2/6-31+G*	2.80 ± 0.79	979 ± 276	$\cdots$	$\cdots$
MP2/6-311++G(2d,p)	2.40 ± 0.56	839 ± 196	$\cdots$	$\cdots$
MP2/6-311++G(3df,2p)	2.59 ± 0.61	906 ± 213	$\cdots$	$\cdots$
MP2/DZP++	2.81 ± 0.87	983 ± 304	2.79 ± 0.86	976 ± 301
MP2/TZ2P++	2.33 ± 0.33	815 ± 114	2.30 ± 0.33	804 ± 114

ionization energies for the *ortho* and *meta* species prevents us from determining the binding of water to the corresponding ions. However, a value can be determined for pDFB, where the interaction is ~2.5 times larger than for the neutral complex.

The pDFB-H_2O binding energy limits determined in the REMPI study of Martrenchard *et al.*[14] are included in Table II. For the neutral, our imaging values lie below the lower bounds determined previously while our value for the cation is only within the bounds set because they include the uncertainty in the ionization energy of the complex. The lower bound set by Martrenchard *et al.* is too high. It was deduced from the failure to observe dissociation from the ion after 1+1 REMPI via $\overline{6}_0^1$. When considering dissociation from the ion, not all of the energy provided by the two photons need reside in the ion. A distribution of population will be produced in the ion, governed by the Franck–Condon factors for the ionization process, and the photoelectron will remove any excess energy. By this means, it is possible to have situations where the photon energy absorbed exceeds the dissociation limit, but dissociation is not observed as the ions are only formed in vibrational levels below dissociation. It appears that this is the situation for excitation of pDFB-H_2O via $\overline{6}_0^1$.

The fluorine substitution on the aromatic ring leads to a different binding site (in-plane to F) compared to that for the parent system benzene-H_2O (B–H_2O; out of plane to the π-electron system). It is thus interesting to compare the DFB-H_2O binding energies with that for B–H_2O. The most precise determination of the S_0 binding energy for B–H_2O has reported 853 ± 32 cm^{-1}.[5,21] The S_0 binding energies for the DFB-H_2O complexes are 891 ± 4, 945 ± 10, and 922 ± 10 cm^{-1} for o-, m-, and p-DFB. The DFB-water values are 4.5%, 10.8%, and 8.1% larger for o-, m-, and p-DFB, respectively. Although there is a net destabilizing of the aromatic benzene system by the addition of fluorine, there is π back bonding which increases the electron density in the ring,[6] which suggests that the out-of-plane interaction might be enhanced in the DFBs compared with benzene. While the three DFB-H_2O binding energies are larger than the B–H_2O value, the increase is quite small, suggesting that the in-plane configuration is only marginally lower in energy than the out-of-plane one. The increase in binding energy for oDFB-H_2O is particularly small suggesting that there is little difference in energy between the in-plane and out-of-plane geometries in this case.

While the S_0 binding energies for the DFB-H_2O com-

plexes are uniformly larger than the B–H_2O value, this is not the case for the S_1 values. The S_1 values are B–H_2O 803 ± 32 cm^{-1}, oDFB-H_2O 786 ± 4 cm^{-1}, mDFB-H_2O 853 ± 10 cm^{-1}, and pDFB-H_2O 753 ± 10 cm^{-1}. The oDFB-H_2O and pDFB-H_2O values are smaller than the B–H_2O value. This raises the interesting possibility that the out-of-plane geometry is favored in the S_1 state for the oDFB-H_2O and pDFB-H_2O complexes. Excitation may not access the global minimum in the S_1 state of these complexes since the Franck–Condon factors will favor excitation to the in-plane geometry which may simply be a local minimum. These systems would be excellent candidates for high level *ab initio* calculations to investigate this issue.

Calculations have not been reported for the dissociation energies of the mDFB-H_2O and oDFB-H_2O complexes; however, they have been published for pDFB-H_2O (Ref. 9) and these are summarized in Table V. The calculations were all at the MP2 level of theory but varied with respect to basis set. Within the quoted theoretical uncertainty all of the basis sets give a value matching the experimental value although the MP2/6-311++G(3df,2p) value is closest.

B. Recoil energy distributions

The recoil energy distributions for the three vibrational levels of pDFB-H_2O are displayed in Fig. 3 with the intensity on a logarithmic scale. A distribution for the dissociation of pDFB-Ar from the $\overline{3^1 5^1}$ level has been included for com-
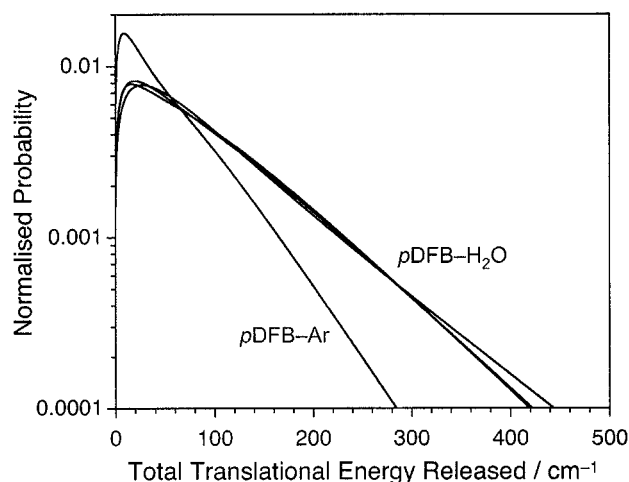

FIG. 3. A comparison of the recoil distributions for pDFB-H_2O with a representative distribution for pDFB-Ar.
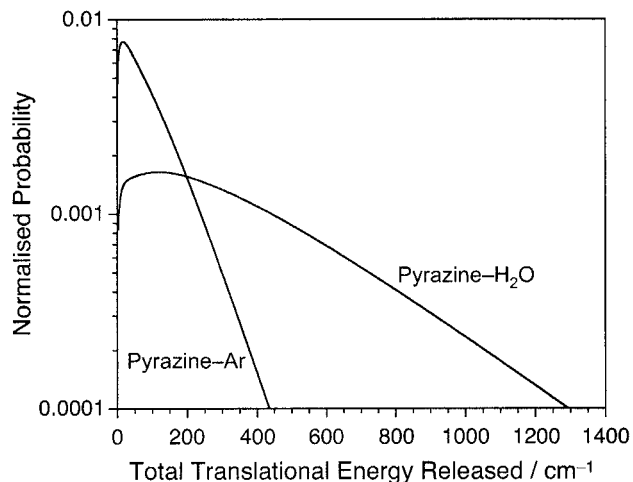
FIG. 4. Recoil distributions for dissociation of pyrazine-H$_2$O and pyrazine-Ar from the T_1 state (obtained from the data given in Ref. 12). The initial T_1 vibrational energy is 4056 cm^{-1}. Comparison with Fig. 4 shows how much broader these distributions are compared with the pDFB-H$_2$O case.

parison. The S_1 pDFB-Ar recoil distributions are all very similar, so the 3^15^1 distribution is representative of this complex.[11] The pDFB-H$_2$O distributions are very similar as a group, although clearly different to the Ar case, showing a larger proportion of molecules with higher translational energy release.

Recoil energy distributions for dissociation occurring within the triplet state (T_1) of a number of aromatic van der Waals clusters have been determined using a velocity resolved time-of-flight technique by Yoder and Barker.[12] Figure 4 shows translational energy distributions obtained by these authors for the dissociation of pyrazine-Ar and pyrazine-H$_2$O clusters, reproduced from the data provided in their paper. A long tail to significantly higher energy occurs in the distribution for the pyrazine-H$_2$O complex compared with the pyrazine-Ar complex. Interestingly, the pyrazine-Ar distribution is indistinguishable from the pDFB-H$_2$O distributions. Experiments indicate that pyrazine-H$_2$O contains a hydrogen bond between one of the hydrogen atoms on the water molecule and a nitrogen atom in the pyrazine ring.[23] Similar to the pDFB-H$_2$O complex, the water molecule lies in the plane of the ring.

Yoder and Barker have postulated that the difference in the distributions for the pyrazine-Ar and pyrazine-H$_2$O clusters is due to the distinction between hydrogen bonding and nonlocalized dispersive van der Waals interactions. The relatively weak dispersive interactions in aromatic-Ar means the argon molecule is able to migrate over the aromatic ring. Trajectory calculations on the pyrazine-Ar complex[24] have shown that, as energy is transferred from the initially excited pyrazine vibrations to the intermolecular modes, the Ar atom samples other minima on the surface until the energy in the intermolecular modes exceeds the binding energy and the molecule dissociates. For pyrazine-water, Yoder and Barker suggest that since a hydrogen bond between the water molecule and a lone pair of electrons on a highly electronegative atom is localized; no change in geometry of the cluster occurs without breaking the bond. They have argued that this

allows more energy to be partitioned into translational energy rather than rotational energy of the fragments because the initial geometry of the cluster is constrained prior to dissociation.

The distributions reported by Yoder and Barker reveal average recoil energies of 100 and 111 cm^{-1} for their two pyrazine-Ar distributions and 425 cm^{-1} for pyrazine-H$_2$O.[12] Our velocity map imaging measurements of pDFB van der Waals molecules give average recoil energies of ~62 and ~100 cm^{-1} for Ar and H$_2$O clusters, respectively. More energy is released as translational energy in dissociation of the pDFB-H$_2$O cluster relative to the Ar cluster, but the increase is only ~60%, far from the ~400% increase seen in the pyrazine case.

The reason for the much higher average translational energy release for the pyrazine–H$_2$O complex compared to pDFB-H$_2$O is unclear. The major differences between the pyrazine cluster dissociation and our measurements for pDFB are that dissociation of the pyrazine clusters is from the lowest triplet state and involves much higher energies. Prior to dissociation the vibrational energy of pyrazine clusters is 4056 cm^{-1}. Although the dissociation energy is not known for this case, and hence the excess energy is unknown, it is clearly well above the ~1300 cm^{-1} available for the highest vibrational level we have investigated for pDFB-H$_2$O. However, for pDFB-Ar we found that there is essentially no change in the average translational energy released with increasing initial vibrational energy[11] and the limited data set for the water complex also shows no change with increasing vibrational energy. We thus believe it unlikely that the differences arise from the extra vibrational energy available for pyrazine-water.

Previously, we have noted that the dissociation of aromatic–rare gas complexes leads to significant rotational excitation of the aromatic fragment.[20,25] It appears that this is also the case for dissociation of pDFB-H$_2$O complexes. Consider dissociation from $\overline{3^1}$. $\overline{3^1}$ is 490 cm^{-1} above dissociation, so this is the maximum energy available to the products. 490 cm^{-1} is well below the water vibrations and the excess energy will appear as translation of the pDFB and H$_2$O fragments, rotation of water and pDFB, and vibration of pDFB. Few vibrational levels of pDFB are accessible.[22] The recoil energy distribution, however, shows no structure, particularly at high translational energy, which corresponds to low vibrational energy where there is a large gap between vibrational levels. This lack of structure indicates significant rotational excitation of pDFB and/or water fragments.

V. CONCLUSIONS

We have determined the binding energies of the pDFB-H$_2$O, mDFB-H$_2$O, and oDFB-H$_2$O complexes. The ground state binding energies for the three difluorobenzene isomers with water are very similar, varying by ~6.5%. This lack of variation is circumstantial evidence for water binding to the three isomers via the same interaction. Based on the established binding for pDFB-H$_2$O,[7] we suggest that in all cases water forms an in-plane O–H···F hydrogen bond to one of the fluorine atoms on the ring, with a weaker interac-

tion of the water O atom with an *ortho* hydrogen, although we cannot rule out an interaction of the water H with the second F atom in the *ortho* and *meta* cases. The ground state binding energies for the DFB-H_2O complexes are about 5%–11% larger than that for benzene-H_2O. However, in the S_1 state the binding energies of the *o*- and *p*-difluorobenzene-H_2O complexes are smaller than the benzene-H_2O value, raising an interesting question about whether the geometry at the global energy minimum remains in-plane in the excited electronic states of these two complexes.

Distributions for the kinetic energy released in the dissociation of *p*DFB-H_2O have been measured from the $\overline{3^1}$, $\overline{5^2}$, and $\overline{3^1 5^1}$ levels of the excited electronic state. These levels are 490, 880, and 1304 cm^{-1}, respectively, above the dissociation threshold. Within the experimental uncertainty, the translational energy distributions are the same for dissociation from $\overline{3^1}$, $\overline{5^2}$, and $\overline{3^1 5^1}$. The corresponding average recoil energies were determined to be 101, 100, and 97 cm^{-1}, respectively. The majority of the energy remains as vibrational and rotational energy of the fragments. The lack of structure in the recoil distribution for dissociation from $\overline{3^1}$ indicates that there is significant rotational excitation in the fragments. For the relatively low initial vibrational energies studied, there is no change in translational energy released with increasing internal energy of the excited complex. At the energies investigated, no long tail was observed in the distributions as was observed in a previous study of the translational energy released in dissociation of a hydrogen bonded complex.[12]

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