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The binding energy of Ar to *p*-difluorobenzene–Ar. How large are three-body effects in *p*-difluorobenzene–Ar₂?

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Abstract

The technique of velocity map imaging has been used to determine the dissociation energy for the process *p*-difluorobenzene–Ar₂ \rightarrow *p*-difluorobenzene–Ar + Ar. The aim of the experiment was to obtain a value for comparison with the dissociation energy for the process *p*-difluorobenzene–Ar \rightarrow *p*-difluorobenzene + Ar in order to ascertain the extent of three-body effects. We find that the dissociation energy for the loss of an Ar atom from *p*-difluorobenzene–Ar₂ is $339 \pm 3 \text{ cm}^{-1}$, which is the same within experimental uncertainty as that for the loss of Ar from *p*-difluorobenzene–Ar ($337 \pm 4 \text{ cm}^{-1}$). We conclude that the presence of the first Ar affects the binding energy of the second by ~2% or less. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

Van der Waals molecules provide a means to investigate solvation. The effects of the solvent can be modelled by adding atoms or molecules sequentially to create larger clusters. Fundamental properties of interest are the binding energies of the successive 'solvent' species to the 'solute' molecule and the extent to which many-body effects are operative.

In the case of aromatic–rare gas complexes, it is usual for the first rare gas atom to sit above the aromatic ring, and for the second to take an equivalent position on the opposite side of the ring [1-5]. (Such structures are referred to as (1|1)complexes; structures with both atoms are on the same side of the aromatic are referred to as (2|0)complexes.) As a result, the spectroscopic shifts are essentially doubled when the second atom is added and, indeed, the observation of a doubling of the spectroscopic shift is experimental evidence that two atoms occupy equivalent sites [5-9]. (This is referred to as the addition rule.) In the event that the interaction of the second atom is not influenced by the first, i.e., three-body effects are negligible, the binding energies will be the same. However, if the second atom is influenced by the presence of the first, the binding energy for the process $A-R_2 \rightarrow A-R+R$ will differ from that for $A-R \rightarrow A + R.$

There is some evidence that three-body effects, while small, are observable in (1|1) aromatic-rare gas complexes, i.e., the presence of the first rare gas

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atom has a small but measurable affect on the interaction of the second so that it is slightly different to the interaction of the first rare gas species with the bare aromatic. For example, the addition rule indicates that the ionization potential of the complex should be shifted equal amounts for each atom occupying an equivalent position. For fluorobenzene– Ar_2 , the shift in ionization potential from that of fluorobenzene is 422 cm⁻¹ [10,11], which is slightly less than twice the shift for fluorobenzene-Ar (reported as 227 cm⁻¹ [10] or 223 cm⁻¹ [11]). The reduction from the 'addition rule' value is 5-7%. Lembach and Brutschy [11] have reported similar upper limits to the binding energies for removal of an Ar atom from fluorobenzene-Ar and fluorobenzene-Ar₂ (344 and 347 cm⁻¹, respectively). Unfortunately, as only upper limits are available, the effect of three-body effects on the binding energy has not been determined. Theoretical calculations of the binding energies of benzene-Ar and benzene-Ar2 predict that the binding energy of the first and second Ar atoms are not equal. Hobza and co-workers calculate the stabilization energy of benzene–Ar to be 649.2 cm^{-1} , while that of benzene–Ar₂ is 1324.7 cm⁻¹, indicating that the binding energy of Ar to benzene-Ar is 4% larger than that for Ar to bare benzene [12].

We have recently reported the dissociation energy for the *p*DFB–Ar complex, measured using the technique of velocity map imaging [13,14]. The S₁ value was determined to be $367 \pm 4 \text{ cm}^{-1}$. In the present work we present the results of an investigation of the dissociation energy for removal of one Ar from the *p*DFB–Ar₂ complex. As can be seen from the uncertainty limits quoted, we are able to measure the dissociation energy to sufficient precision (~ $\pm 1\%$ at <400 cm⁻¹) that differences in the binding energy of several percent, as suggested by the calculations for the benzene–Ar system, can be observed. The aim of the present study is to determine the extent to which the presence of the first Ar atom influences the binding of the second.

2. Experimental overview

The experimental details and an explanation of the technique used to determine the dissociation energy have been given in previous publications [13–15]. Here we present an overview of the salient features of the experiment. The dissociation energy is measured from the maximum translational energy released in the dissociation. To observe this we require distributions that are truncated from the usual form seen. Because the translational energy release distributions typically peak at low energy ($\sim 20 \text{ cm}^{-1}$) and decay in an exponentiallike fashion to approach zero by $\sim 300 \text{ cm}^{-1}$, to observe a truncation in the distribution it is necessary to initiate dissociation from a vibrational level within $\sim 200 \text{ cm}^{-1}$ of the dissociation energy. Since the velocity map imaging process measures fragment velocity, and the kinetic energy depends on the square of the velocity, the energy resolution is best at low translational energy.

The experiment is performed by exciting $pDFB-Ar_2$ to an S₁ vibrational level above, but near to, the dissociation energy, which will be similar to that for pDFB-Ar. If the complex dissociates from this level sufficiently rapidly, the pDFB-Ar product is formed within the duration of the laser pulse and can absorb a photon and ionize. The $pDFB-Ar^+$ ions so produced are detected using the velocity map imaging technique [16] with an ion counting configuration for the data collection, which enhances the resolution [17]. Depending on the internal energy with which they are produced, some of the $pDFB-Ar^+$ ions may dissociate, however this does not influence the measurement (apart from a depletion in the $pDFB-Ar^+$ signal) since only $pDFB-Ar^+$ ions are detected. (The dissociation of higher clusters does not confound the $pDFB-Ar^+$ detection since they are excluded in the initial $S_1 \leftarrow S_0$ excitation step.) Should $pDFB-Ar_2$ dissociate slowly from the S₁ level chosen, it may be ionized intact and subsequently dissociate from a state of the ion to produce $pDFB-Ar^+$. Thus the $pDFB-Ar^+$ signal can arise from dissociation in S_1 or D_0 and one needs to be careful to distinguish the two processes.

A number of transitions of the $pDFB-Ar_2$ complex have been identified in studies of the pDFB-Ar complex [18,19]. Typically these transitions are red-shifted by 60 cm⁻¹ from those of pDFB. However, for out-of-plane modes the shifts are often reduced. We have obtained translational energy distributions for dissociation of the *p*DFB– Ar₂ complex after exciting the $\overline{8_0^2}$ and $\overline{6_0^1}$ transitions. v_8 is the out-of-plane mode most affected by the <u>fo</u>rmation of the van der Waals complex and the $\overline{8_0^2}$ transition is red-shifted by 34 cm⁻¹. The $\overline{6_0^1}$ transition is red-shifted by 60 cm⁻¹. The $\overline{6_0^1}$ transition is 23 cm⁻¹ higher in energy than the $\overline{8_0^2}$ transition. *p*DFB and *p*DFB⁺ frequencies are given in [20].

When observing $pDFB^+$ ions from the dissociation of pDFB-Ar a background is observed in the centre of the images due to non-resonant ionization of uncomplexed pDFB in the molecular beam [13,14]. This prevents observation of the lowest velocity fragments. A feature of monitoring pDFB-Ar⁺ ions from pDFB-Ar₂ dissociation is that this background is absent and the low energy end of the distributions for pDFB-Ar₂ dissociation are therefore well defined.

3. Results and discussion

Translational energy distributions for dissociation following excitation via the $\overline{8_0^2}$ and $\overline{6_0^1}$ transitions are presented in Figs. 1 and 2, respectively. The distribution obtained after exciting the $\overline{8_0^2}$ transition appears to consist of two components, a very sharp initial spike and an underlying expo-



Fig. 1. The distribution of total translational energy released \underline{in} the dissociation of *p*DFB-Ar₂ following excitation of the $\overline{8_0^2}$ transition.



Fig. 2. The distribution of total translational energy released \underline{in} the dissociation of *p*DFB–Ar₂ following excitation of the $\overline{6_0^1}$ transition. The points are the experimental data while the solid line is a fit to the data of the form given in Eq. (1).

nential-like decay. The distribution following excitation of the $\overline{6_0^1}$ transition decays in an exponential-like fashion and has essentially dropped to zero at ~300 cm⁻¹. The solid line is the fit to the distribution by a function of the form

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

which we have shown previously to provide a good fit to the translational energy release distributions [15].

In the <u>case</u> of the distribution obtained by exciting the 6_0^1 transition, it is clear that dissociation is occurring within the $pDFB-Ar_2^+$ ion rather than from the $\overline{6^1}$ level within S₁. If dissociation were occurring from 6¹ we would see a truncated distribution similar to that observed for the 6¹ level of the *p*DFB–Ar complex. Unfortunately, due to the weak signal for the pDFB-Ar₂ complex, photoelectron images could not be used to identify the vibrational states populated in the cation. ZEKE spectra of pDFB indicate that at the wavelength of the $\overline{6_0^1}$ transition there is sufficient excess energy from two photons (~979 cm⁻¹) to populate the $\overline{5_1}$ and $\overline{6_2}$ levels in the cation [20]. These levels are $\sim 264 \text{ cm}^{-1}$ and $\sim 308 \text{ cm}^{-1}$, respectively, above the D_0^+ dissociation limit for the loss of one Ar atom ($D_0^+ \cong 572 \text{ cm}^{-1}$) estimated from the value for dissociation of the *p*DFB–Ar⁺ complex [14]. Based on ZEKE photoelectron spectra for *p*DFB, the $\overline{6_2}$ level should be the major vibrational level populated in the cation following the excitation of the $\overline{6_0}$ transition. The majority of fragments should be produced with ~310 cm⁻¹ of excess energy, consistent with the distribution observed.

The exponential-like decay observed in the $\overline{8_0^2}$ distribution resem<u>bles</u> the distribution measured after exciting the $\overline{6_0^1}$ transition. We also attribute this to dissociation in the cation ground state from levels well above the dissociation energy in this state. The initial sharp decay is attributed to dissociation in S₁. As discussed above, the binding energies for one Ar atom in *p*DFB–Ar₂ and the *p*DFB–Ar complex should be similar. On this basis, for *p*DFB–Ar₂ we expect up to ~19 cm⁻¹ will be released as translational energy of the fragments.

To obtain a value of the binding energy of the $pDFB-Ar_2$ complex in the S₁ state, we have determined the contribution to the $\overline{8_0^2}$ distribution from dissociation in the S₁ state by removing the contribution from dissociation in the D₀ state as follows. Since the exponential-like decay appears the same in both the $\overline{6_0^1}$ and $\overline{8_0^2}$ images, we subtracted the fit to the $\overline{8_0^2}$ distribution. The resulting distribution is shown in Fig. 3. This approach is reasonable as we have found in the case of pDFB-Ar that the translational energy release distributions are essentially the same for dissociation from a wide variety of S₁ levels [21].

The maximum translational energy in the distribution in Fig. 3 is $18 \pm 3 \text{ cm}^{-1}$. For the *p*DFB– Ar₂ complex, the energy of the $\overline{8^2}$ level in S₁ is 387 cm^{-1} . Therefore the binding energy for the *p*DFB–Ar₂ complex for the loss of one Ar atom in S₁ is $369 \pm 3 \text{ cm}^{-1}$. Within experimental error this is the same as the binding energy for the *p*DFB–Ar complex ($367 \pm 4 \text{ cm}^{-1}$) [14]. For comparison, a 4% increase from the dimer to the trimer, as calculated by Hobza [12] for benzene–Ar₂ vs. benzene–Ar, would yield a value of 382 cm^{-1} . There is a 30 cm⁻¹ red-shift in the S₁–S₀ transition from *p*DFB–Ar to *p*DFB–Ar₂ [18,19], so the binding energy in the S₀ state is $339 \pm 3 \text{ cm}^{-1}$. The ionization potential of the *p*DFB–Ar₂ complex is not



Fig. 3. The contribution from dissociation in S₁ to the total translational energy released to the *p*DFB–Ar and Ar fragments following dissociation from the $\overline{8^2}$ level. The distribution was obtained by subtracting the fit to the $\overline{6_0^1}$ distribution shown in Fig. 2 (appropriately scaled) from the $\overline{8^2}$ distribution shown in Fig. 1.

known and hence we cannot give a value for the binding energy in the D_0 state. However, the ionization potential of the complex is likely to be shifted by almost equal amounts for each atom occupying an equivalent position ($\Delta IP = 237 \pm$ 5 cm⁻¹ for *p*DFB–Ar [22]), and so the binding energy in the D_0 state is expected to be ~576 cm⁻¹.

This result reveals that the binding of the second atom in the $pDFB-Ar_2$ complex is influenced by the presence of the first Ar atom on the other side of the aromatic ring by $\sim 2\%$ or less. Threebody effects in this system are clearly quite small. While any effect was expected to be small, a value of less than $\sim 2\%$ is interesting given the 5–7% shift seen in the ionization potential for the closely related fluorobenzene-Ar/fluorobenzene-Ar₂ systems and the 4% change calculated by Hobza and co-workers for the benzene-Ar and benzene-Ar₂ systems. It is clearly of interest to investigate this effect in a number of (1|1) aromatic-rare gas complexes to ascertain the range in magnitude of three-body effects in these systems, and to extend such measurements to (2|0) complexes.

It is interesting to note the apparent slowing of dissociation at the 6^1 level between the *p*DFB–Ar and *p*DFB–Ar₂ complexes. For *p*DFB–Ar, dissociation in S₁ is rapid from $\overline{6^1}$ and the translational

energy distributions are dominated by S₁ dissociation [13,14]. For pDFB-Ar2, however, dissociation from $\overline{6^1}$ is sufficiently slow that the translational energy release images are dominated by dissociation in D_0 . The dissociation rate from $\overline{8^2}$ is greater than from $\overline{6^1}$ despite $\overline{6^1}$ being of higher energy. Jacobson et al. [18] have measured the dissociation rate from a number of S_1 levels in the pDFB-Ar complex and found that dissociation occurs non-statistically. They did not find a trend in the rate of dissociation with increasing energy of the vibrational levels they investigated. For example, dissociation from the $\overline{6^1}$ level was found to occur faster than from $\overline{6^2}$ and the rate of dissociation from $\overline{5^1}$, which is 3 cm⁻¹ lower in energy than $\overline{6^2}$, is also greater than from $\overline{6^2}$. The *p*DFB-Ar₂ complex appears to behave similarly. Intramolecular energy flow within the van der Waals molecule is the precursor to dissociation taking place. Initially, IVR populates a combination of chromophore and intermolecular vibrational levels. The IVR rate is determined by coupling strengths and vibrational state densities. The different dissociation rates in the two complexes at the 6¹ level and the more rapid dissociation from $\overline{8^2}$ compared to $\overline{6^1}$ in the trimer is most probably a consequence of the relatively low density of states at these energies and hence the role of accidental resonances in determining IVR rates.

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