

# Testing the morphed potential of Ar:HBr using frequency and phase stabilized FASSST with a supersonic jet

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Received 26 September 2002; in final form 30 December 2002

## Abstract

The lowest frequency  $\Sigma$  bending vibration of Ar:HBr has been recorded using frequency and phase stabilized Fast Scan Submillimeter Spectroscopic Technique (FASSST) coaxially with a supersonic jet. The fitted band origin was  $\nu_0 = 329611.4482(16)$  MHz, the excited state rotational constant was  $B = 1236.41359(22)$  MHz, the distortion constants were  $D_J = 0.0124740(36)$  MHz and  $H_J = -2.503(17) \times 10^{-6}$  MHz and the quadrupole constants were  $\chi_{aa} = 260.9552(79)$  MHz and  $D_K = -0.03174(35)$  MHz for Ar:H<sup>79</sup>Br. Corresponding values have also been determined for the Ar:H<sup>81</sup>Br isotopomer.  $\chi_{aa}$  and  $D_K$  are compared with values predicted from a recently determined morphed potential of Ar:HBr.

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## 1. Introduction

There recently has been interest in determining potential energy surfaces for weakly bound molecular complexes using morphing methods based on ab initio calculation [1–5]. The objective of this approach has been to generate morphed potentials that are more precise and reliable model representations of the actual potentials of these weakly bound species than can be generated solely on the basis of ab initio calculation or by fitting simple functional forms. Transformations that involve shifting and scaling of potentials

calculated from ab initio calculation have been used to generate morphed potentials that give the best agreement with available experimental data especially those from high resolution spectroscopic methods. Following initial studies of Ne:HF [1] and Ar:HI [2], a full dimensional morphed potential was determined for Ar:HBr [3] using optimization to available high resolution rotational and rovibrational spectroscopic data. Interestingly, the generated morphed potential demonstrated that the ground state structure of the complex was hydrogen bonded, Ar:HBr but different from the global minimum van der Waals Ar:BrH structure. This result is contrary to an oft-held tenet of molecular structure that the ground and global minimum structures of molecular species have atoms that are similarly

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bound. It is thus important to test the accuracy of this morphed potential of Ar:HBr by generating additional precise data not included in the original fit so that this new information can be used to provide independent and stringent tests for such a model potential and to further optimize that potential. The initial microwave analysis of Ar:HBr using pulsed nozzle FT microwave spectroscopy by Flygare and coworkers [6] provided highly accurate ground state complex parameters including  $B_0$ ,  $D_J^0$ ,  $\chi_{aa}^0$  and  $D_\chi^0$  together with  $c_0$ , and lead to the conclusion that the ground state of the complex was bound through the proton of HBr. Howard and coworkers [7–9] and Read and Campbell [10] also carried out radio frequency and additional microwave studies that extended the previous analysis. A later study of the  $Q(J)$  branch in the  $\Pi$  intermolecular bend of the complex was made possible by far infrared difference frequency laser spectroscopy [11]. An extensive near infrared high frequency supersonic jet spectrum [12] of Ar:HBr in the fundamental HBr stretch and its intermolecular combination and hot bands subsequently provided sufficient spectroscopic data to enable the generation of a fully vibrational morphed potential for the complex [3]. Certain characteristics of the latter model potential were in contrast to the other previously reported potentials whether based on ab initio calculations [13] or available spectroscopic data [9,14]. The previous experimental studies, however, did not provide spectroscopic data for the  $\chi_{aa}$  and  $D_\chi$  values of the  $\Sigma$  bending vibration. As pointed out by Flygare and coworkers [6], the latter can provide a sensitive test of the intermolecular potential in Ar:HBr.

We now report a direct absorption analysis of the  $\Sigma$  bending vibration of Ar:HBr using a recently constructed spectrometer exploiting frequency and phase stabilized Fast Scan Submillimeter Spectroscopic Technique (FASST) configured with a coaxial pulsed supersonic jet expansion. The resolution and accuracy of this instrument is sufficient to determine precise values for a number of parameters in both the ground and excited states of the complex, but most importantly for the  $\Sigma$  bending excited state values of  $\chi_{aa}$  and  $D_\chi$ . Such results will then be

available for comparison with predictions based on the previously generated morphed potential of Ar:HBr, thus providing an independent means of evaluating and verifying the quality of that potential. Furthermore, this information can provide additional accurate data that can be used to further optimize the morphed potential of Ar:HBr.

## 2. Experimental

Selected transitions in the range  $P(12)$  to  $R(10)$  were recorded for the  $\Sigma$  bending vibration in both Ar:H<sup>79</sup>Br and Ar:H<sup>81</sup>Br isotopic species. Spectra were recorded with direct absorption in a supersonic nozzle expansion using a coaxial frequency and phase stabilized FASSST. Details concerning the spectrometer will be published elsewhere [15], so only a brief description will be provided here. This approach takes advantage of characteristics associated with two recently developed supersonic jet spectrometers: (i) a millimeter-wave spectrometer that used a coaxial jet spectrometer [16] and (ii) FASSST with pulsed supersonic jet expansions [17]. In our spectrometer [15], we exploit the basic coaxial jet design used previously [16] but utilize a frequency and phase stabilized [18] capability exploiting the FASSST approach [17] to replace lock-in detection used in the former design [16]. This submillimeter spectrometer was operated with an OB-30 ISTOK backward wave oscillator in the frequency range 240–360 GHz for the current experiments. The frequency and phase stabilized source, which we have demonstrated [15] to have an instrumental resolution to better than 2 kHz, is scanned in 50 kHz steps over 2 MHz segments with coaddition to provide scans of 40 MHz or more. All currently reported spectra were recorded with 400 coadditions. The frequency precision of the spectrometer was calibrated within 1 kHz against the precisely determined frequencies of the quadrupole components of  $J1 \leftarrow 0^2\text{H}^{79}\text{Br}$  and  $^2\text{H}^{81}\text{Br}$  transitions previously recorded in a molecular beam [19]. The spectrometer was computer controlled with Lab-view software adapted for the current purposes.

Spectra of the Ar:HBr complex were recorded in a pulsed nozzle expansion from a reservoir with 1.6% HBr and 98.4% Ar composition using an InSb hot electron bolometer operated at liquid helium temperatures. The expansion involved a stagnation pressure of 40 psi through a 100  $\mu$ m diameter nozzle at 20 Hz repetition rate with a pulse duration of 1.5 ms. The vacuum system consisted of a Varian 400 M diffusion pump backed by a Leybold RUVAC WA-251 Roots blower and a 1398 Welch mechanical pump.

### 3. Analysis

The quadrupole substructure of the  $\Sigma$  bending vibration of both ArH<sup>79</sup>Br and ArH<sup>81</sup>Br were predicted on the basis of ground state parameters [6] and predictions of the  $\Sigma$  state parameters based on the previous morphed potential [3]. Quadrupole components were readily identified within 25 MHz of prediction and measured for selected transitions in the range  $P(12)$  and  $R(10)$  (see Fig. 1). Transitions frequencies were then fitted with all parameters optimized in a non-linear least squares fit using the expression [20].

$$\nu = \bar{\nu}_0 + E'(J', I', F') - E_0(J, I, F), \quad (1)$$

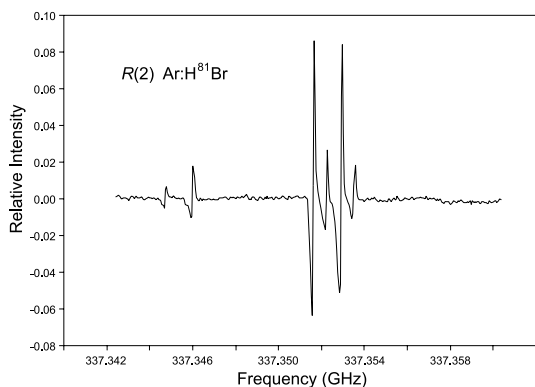


Fig. 1. A segment of the quadrupole resolved submillimeter spectrum in the  $\Sigma$  vibration of Ar:H<sup>81</sup>Br showing the  $R(2)$   $F' \leftarrow F''$   $5/2 \leftarrow 5/2$ ,  $9/2 \leftarrow 7/2$  and  $3/2 \leftarrow 1/2$  substructure centered at 337345.4290, 337352.3420 and 337352.9480 MHz, respectively. The spectrum represents coaddition of 400 individual scans. Each transition appears as a Doppler doublet. The absolute accuracy of the transition center frequencies are estimated to be better than 50 kHz.

Table 1  
Referenced and fitted data for  $\Sigma$  bending vibration

State	Exp <sup>a</sup>	$\nu_0$ (MHz)	$B$ (MHz)	$D_J$ (MHz)	$H_J$ (MHz)	$\chi_{aa}$ (MHz)	$D_K$ (MHz)
<i>Ar:H<sup>79</sup>Br</i>							
$\Sigma$ bend state	A	329611.4482(16)	1236.41359(22)	0.0124740(36)	$-2.503(17) \times 10^{-6}$	260.9550(79) <sup>b</sup>	$-0.03174(35)$
$\Sigma$ bend state	B	329618.0(39)	1236.317(39)	0.01230(13)	$-2.37(12) \times 10^{-6}$		
Ground state	A		1106.67057(19)	0.0124789(32)	$1.478(14) \times 10^{-6}$	173.2466(79)	0.01735(33)
Ground state	C		1106.66951(17)	0.01239(4)		173.199(6)	0.01842(26)
Ground state	D		1106.67018(20)	0.01241(1)		173.2209(46)	0.01763(3)
<i>Ar:H<sup>81</sup>Br</i>							
$\Sigma$ bend state	A	329225.6995(15)	1226.77332(22)	0.0123085(37)	$-2.459(19) \times 10^{-6}$	217.8952(75) <sup>b</sup>	$-0.02619(36)$
$\Sigma$ bend state	B	329253.1(39)	1226.644(45)	0.01218(16)	$-2.34(15) \times 10^{-6}$		
Ground state	A		1097.58118(19)	0.0122791(32)	$1.461(13) \times 10^{-6}$	144.8117(77)	0.014453(35)
Ground state	C		1097.58109(15)	0.01226(3)		144.793(5)	0.0152(23)
Ground state	D		1097.58119(15)	0.01223(3)		144.8067(5)	0.01471(23)

<sup>a</sup> The different experiments are: A, results from experiments presented in this Letter, where the errors represent one standard deviation from fit to Eq. (1); B, data from [12] and references therein; C, ground state molecular parameters from [6]; D, ground state molecular parameters fitted as in [6] with additional data from [9].  
<sup>b</sup> Ratio  $\chi_{aa}(\text{Ar:H}^{79}\text{Br})/\chi_{aa}(\text{Ar:H}^{81}\text{Br}) = 1.19762$  compares with the value  $\chi_{aa}(\text{H}^{79}\text{Br})/\chi_{aa}(\text{H}^{81}\text{Br}) = 1.19705$  [21].

where

$$\begin{aligned}
 E(J, I, F) = & BJ(J+1) - D_J J^2(J+1)^2 \\
 & + H_J J^3(J+1)^3 - [\chi_{aa} + D_\chi J(J+1)] \\
 & \times \left\{ \frac{\frac{3}{4}c(c+1) - I(I+1)J(J+1)}{2I(I-1)(2J-1)(2J+3)} \right\} \\
 & + \frac{[\chi_{aa} + D_\chi J(J+1)]^2}{B} g \times 10^{-3} \\
 & + \frac{c}{2} [F(F+1) - I(I+1) - J(J+1)],
 \end{aligned} \quad (2)$$

where  $B$  is either the relevant ground or excited rotational constant,  $D_J$ ,  $H_J$  corresponding distortion constants,  $\chi_{aa}$  the component of quadrupole constant and  $D_\chi$  the relevant higher order distortion correction to the latter. The remaining  $c$  and  $g$  terms follow the original definitions described in [21]. The results of the fits are given in Table 1 for the significantly determined parameters.

#### 4. Discussion

Analysis of both Ar:H<sup>79</sup>Br and Ar:H<sup>81</sup>Br  $\Sigma$  bending vibrations has been completed varying all parameters in Eqs. (1) and (2). Comparison of the ground state  $B_0$ ,  $D_J$ ,  $\chi_{aa}$  and  $D_\chi$  values determined from the current submillimeter analysis agree within two standard deviations of the mean with the previously recorded pulsed nozzle FT microwave results determined by Flygare and coworkers [6] for the <sup>81</sup>Br isotopic species and also for a comparable fit that included in addition the lower  $J$   $1 \leftarrow 0$ ,  $2 \leftarrow 1$ ,  $3 \leftarrow 2$  transitions from the work of [9]. However, a similar comparison of the ground state constants from the submillimeter with the ground state results for the <sup>79</sup>Br isomeric species showed significant differences compared with the fit of [6]. A fit that included in addition the lower  $J$   $1 \leftarrow 0$ ,  $2 \leftarrow 1$ ,  $3 \leftarrow 2$  transitions from the work of [9] produced a comparable fit as for the <sup>79</sup>Br isotopic species determined from free fitting the submillimeter data. We conclude that the accuracy of the microwave frequency measurements [6] for this latter isotope was high but there were an inadequate variety of transitions and only when addi-

tional microwave [9] data was added was it possible to produce comparably accurate ground state molecular constants. These results indicate that apart from the spin-rotation constant  $c$  which was not significantly determined, all the parameters determined from the current submillimeter data analysis enable determination of the fitted constants to within two standard deviations of those evaluated with the highest microwave accuracy. Such results also indicate that the corresponding excited state parameters can be expected to be determined with comparable accuracy. In addition, we have been able to determine the values of  $H_J$  in both ground and  $\Sigma$  excited state with significant accuracy from analysis of the submillimeter data. Most importantly, the molecular parameters that have been determined for the  $\Sigma$  bending state include the precise determination of  $\chi_{aa}$  and  $D_\chi$  which are now available for comparison with corresponding predictions from a recently completed morphed potential for Ar:HBr [3]. The absolute accuracy of the band origin frequency of  $\nu_0$  is currently expected to be within 50 kHz, although we expect this will be improved in the near future when the instrumental performance is enhanced following instrumental improvements that are currently being implemented. The standard deviation of the Ar:H<sup>79</sup>Br and Ar:H<sup>81</sup>Br fits to the submillimeter data in Table 1 are 4.8 and 5.7 kHz, respectively. These results are for the selected transitions in the range  $P(12)$  to  $R(10)$  that are included in our fits. The molecular parameters and the band origin frequency of the  $\Sigma$  bending state can be seen to be significantly more accurately determined than was possible using predictions based on combination difference frequencies from previously available infrared studies. Most importantly, the accurate values of  $\chi_{aa}$  and  $D_\chi$  for this  $\Sigma$  bending state are now available from experiment. For the hydrogen bonded ground state of the Ar:H<sup>79</sup>Br isotopomer, the value of  $\langle P_2(\cos \theta) \rangle$  from the morphed potential (0.32617) fit the corresponding experimentally determined value of 0.32538 to within 0.3%. The  $\chi_{aa}$  and  $D_\chi$  values are 260.9550(79) and  $-0.03174(35)$  MHz, respectively for the Ar:H<sup>79</sup>Br isotopomer, and correspondingly 217.8952(75) MHz and  $-0.02619(36)$  MHz for the Ar:H<sup>81</sup>Br isotopomer. In the  $\Sigma$  bending state, the

value of  $\langle P_2(\cos \theta) \rangle$  was predicted to be 0.50342 for the Ar:H<sup>79</sup>Br giving a predicted value based on the morphed potential to be  $\chi_{aa} = 267.973$  MHz, an error of +2.7%. The value of  $D_\chi$  predicted from the morphed potential for the Ar:H<sup>79</sup>Br isotopomer was  $-0.03458$  MHz which is within 8.9% of the measured value,  $-0.03174(35)$  MHz. This constant, which predicts the  $J$  dependence of  $\chi_{aa}$ , indicates that with increasing  $J$ , the angle  $\theta$  increases for this effectively van der Waals isomer of the complex. In contrast, the corresponding dependence of the ground state hydrogen bonded complex is opposite corresponding to a decreasing  $\theta$  with  $J$ . Furthermore, the magnitudes of these changes are two times larger in the  $\Sigma$  bending state than in the ground state (see Table 1).

As previously noted [6], in the ground state for ArH<sup>81</sup>Br, the value of  $c$  determined using the relationship  $c = (c_0 \bar{B}/2b) \langle 1 + \cos^2 \alpha \rangle$  gives a value significantly larger than that determined in the fit. As pointed out previously by Flygare and co-workers [6], this value is very sensitive to the frequency accuracy of the microwave measurements and was not well determined in those measurements. As the accuracy of the spectrometer used in the current work is lower by a factor of six, we did not expect to determine this constant with significant accuracy in either state.

The deviations between the observed values of  $\chi_{aa}$  and  $D_\chi$  and those predicted on the basis of the recently morphed potential of Ar:HBr indicate that we should be able to further optimize the modeled potential using the newly generated experimental data. We have thus included this data in such a fit where we have used the same approach as was used in the earlier study of Ar:HBr [3]. In performing this fit, we have added the two new experimental data, the value of  $\langle P_2(\cos \theta) \rangle$  and the value of  $D_\chi$  in the  $\Sigma$  bending state. In the previous study, we used smoothed reducing kernel Hilbert space (RKHS) fitting functions to allow for a more rapid convergence of the various integrals [22]. Unfortunately, these smoothed fitting functions introduced small amplitude oscillations in the resulting interpolated surfaces as can be clearly seen in Fig. 3 of [3]. Thus we initially refit the data used in our previous Letter using no smoothing. This led to a standard deviation with

respect to the experimental data of  $\chi = 1.69$  compared to a fit of  $\chi = 1.50$  found with the smoothed RKHS fitting functions. In all fits presented in this study we have taken the regularization parameter  $\gamma = 10.0$  and the estimated computational uncertainties,  $\sigma$ , were the same as in the previous work with the addition of  $\sigma = 0.002$  for  $\langle P_2(\cos \theta) \rangle$  and  $\sigma = 3.5 \times 10^{-4}$  MHz for the value of  $D_\chi$  in the  $\Sigma$  bending state. We then performed a fit of all the data using the parameters that were used in the original study and obtained a fit with  $\chi = 2.15$ . In this fit, two of the parameters,  $C_{1,1,1}$  (a coupling term between an overall scaling of the potential and stretching of the HBr bond) and  $C_{2,3,0}$  (a term which scaled the Ar–Br distance  $R$  with a term dependent on  $P_3(\cos \theta)$  where  $\theta$  is the H–Br–Ar angle) were not well determined. We removed those two parameters and replaced them with  $C_{3,3,0}$  and  $C_{3,4,0}$  which are  $R$  shifting transformations dependent on  $P_3(\cos \theta)$  and  $P_4(\cos \theta)$ . With the substitution of these two parameters, the surface was fit again yielding  $\chi = 1.80$ . The resulting optimized parameters are given in Table 2 with the parameters of the original fit and the two-dimensional potential with  $r = r_e$  is shown in Fig. 2. At  $r = r_e$  the global minimum was the van der Waals structure with  $V(R' = 3.61 \text{ \AA}, \theta' = 180^\circ) = -172.1 \text{ cm}^{-1}$  with a local minimum in the hydrogen bonded structure with  $V(R' = 4.18 \text{ \AA}, \theta' = 0^\circ) = -148.4 \text{ cm}^{-1}$ . This leads to a difference in the two minima  $\Delta V = V(R' = 3.61 \text{ \AA}, \theta' = 180^\circ) - V(R' = 4.18 \text{ \AA}, \theta' = 0^\circ) = 23.7 \pm 2.7 \text{ cm}^{-1}$ , where the uncertainty is estimated from the statistical uncertainties shown in Fig. 2. This is slightly different from the values previously published which had a global minimum at  $V(R' = 3.59 \text{ \AA}, \theta' = 180^\circ) = -165.4 \text{ cm}^{-1}$  with a local minimum in the hydrogen bonded structure with  $V(R' = 4.18 \text{ \AA}, \theta' = 0^\circ) = -144.5 \text{ cm}^{-1}$ , leading to a difference in the two minima  $\Delta V = V(R' = 3.59 \text{ \AA}, \theta' = 180^\circ) - V(R' = 4.18 \text{ \AA}, \theta' = 0^\circ) = 20.9 \pm 1.9 \text{ cm}^{-1}$ .

The previously published morphing parameters and the current parameters cannot be directly compared since the parameter sets are different and the parameters are not totally linearly independent. Nonetheless, we note that the uncertainties in the parameters are all less than were found in our previous results. All of the parameters are

Table 2

Optimized morphing parameters  $C_{\alpha,i,j}$  and their corresponding uncertainties obtained using the additional data reported in this study compared to those in the earlier study [3]

$(\alpha, i, j)$	From [3]		This study	
	$C_{\alpha,i,j}$	$\sigma$	$\sigma C_{\alpha,i,j}$	$\sigma$
(1,0,0)	1.1321	0.0489	1.2159	0.0241
(1,1,0)	0.0283	0.0042	0.0364	0.0031
(1,2,0)	0.0401	0.0110	0.0062	0.0057
(1,3,0)	−0.1289	0.0055	−0.1477	0.0045
(1,4,0)	−0.0614	0.0107	−0.0735	0.0081
(1,1,1)	−0.0397	0.0353	—	—
(2,0,0)	1.2503	0.0446	1.1778	0.0204
(2,1,0)	−0.0328	0.0148	0.0474	0.0053
(2,2,0)	−0.0456	0.0265	−0.0650	0.0202
(2,3,0)	0.1954	0.0398	—	—
(3,0,0)	0.0506	0.0006	0.0515	0.0005
(3,1,0)	−0.0288	0.0017	−0.0295	0.0009
(3,2,0)	−0.0164	0.0012	−0.0263	0.0017
(3,3,0)	—	—	0.0105	0.0016
(3,4,0)	—	—	0.0141	0.0021
(3,0,1)	−0.0791	0.0036	−0.0717	0.0029
(3,1,1)	−0.0761	0.0052	−0.0827	0.0032

within three times  $\sigma$  of the corresponding values given previously, except for  $C_{2,1,0}$  and  $C_{3,2,0}$ . In each the exceptions, a higher order term of the same type has been removed in the new set of parameters leading to a readjustment of the values

in the lower order term due to correlations between the terms in the previous fit.

We also considered fits where additional parameters were added to the morphing transformation. In each case the fit became somewhat better,

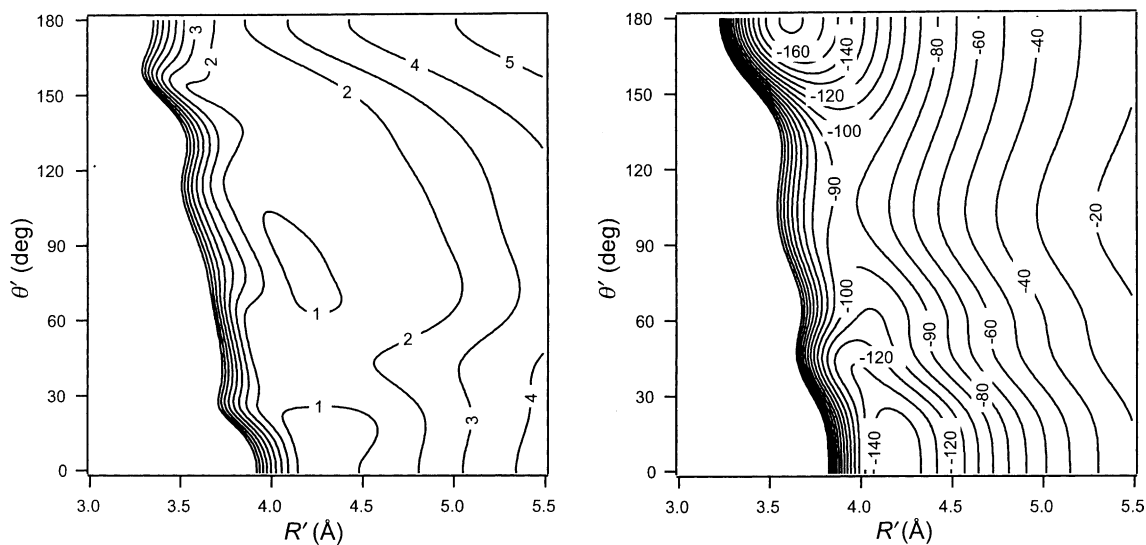


Fig. 2. The morphed interaction potential (right panel) of Ar:HBr and the corresponding uncertainties (left panel) with  $r(\text{H}-\text{Br}) = r_e = 1.4144 \text{ \AA}$ . All contour values are given in the units of  $\text{cm}^{-1}$ . The coordinates  $R'$  and  $\theta'$  are the Jacobi coordinates of the Ar:H<sup>79</sup>Br isotopomer. The uncertainties are for the potential energy relative to the value of the potential energy at the local minimum in the hydrogen-bonded geometry.

although the uncertainties in the resulting potential increased. For example, in one fit we added five parameters,  $C_{1,5,0}$ ,  $C_{1,0,1}$ ,  $C_{1,1,1}$ ,  $C_{3,5,0}$ , and  $C_{3,2,1}$ . This fit had  $\chi = 1.25$  with a local minimum in the van der Waals geometry at  $V(R' = 3.73 \text{ \AA}, \theta' = 180^\circ) = -163.9 \text{ cm}^{-1}$  with a global minimum in the hydrogen bonded structure with  $V(R' = 4.09 \text{ \AA}, \theta' = 0^\circ) = -173.5 \text{ cm}^{-1}$ . This leads to a difference in the two minima  $\Delta V = V(R' = 3.73 \text{ \AA}, \theta' = 180^\circ) - V(R' = 4.09 \text{ \AA}, \theta' = 0^\circ) = -9.6 \pm 11.3 \text{ cm}^{-1}$ . Although this potential does not definitively indicate the structure of the global minimum, the fact that it has such a large uncertainty would indicate that this potential is less reliable than the potential given in Fig. 2 with the parameters listed in Table 2.

## 5. Conclusion

We have developed a frequency and phase stabilized submillimeter coaxial jet spectrometer for investigating intermolecular vibrations in weakly bound complexes. The performance of the spectrometer has been tested by investigating the lowest  $\Sigma$  bending vibration of Ar:HBr. The values of the spectroscopic constants  $\nu_0$ ,  $B$ ,  $D_J$ ,  $\chi_{aa}$  and  $D_\chi$  of the  $\Sigma$  bending state have been determined with microwave accuracy. The predicted values of  $\chi_{aa}$  based on the previously published morphed potential agree moderately well (within 10%) with the newly determined experimental values. Such discrepancies between the predicted  $\chi_{aa}$  and  $D_\chi$  based on the morphed potential and those determined from experiment indicate that the morphed potential can be further refined by including this experimental data in the fit. Qualitatively the new fit is very similar to that given previously with parameters that have somewhat smaller uncertainties than previously found. In particular, the new potential supports the conclusion that the global minimum in the potential (i.e. the equilibrium structure) has the van der Waals structure, whereas the lowest vibrational state has the hydrogen-bonded structure.

## Acknowledgements

B.A. McElmurry, thanks the Robert A. Welch Foundation for financial support in the form of a

pre-doctoral fellowship. We are also thankful to the National Science Foundation and ARP-THCEB for additional support. W. Jabs, T. Walther, A.L. McIntosh and Z. Wang are thanked for advice and discussion during the development of the spectrometer. We express special thanks to the Vladimir Vax and his group at Institute for Physics of Microstructures RAS, Nizhny Novgorod, Russia for their cooperation and help.

## References

- [1] M. Meuwly, J.M. Hutson, *J. Chem. Phys.* 110 (1999) 8338.
- [2] A. McIntosh, Z. Wang, J. Castillo-Chara, R.R. Lucchese, J.W. Bevan, R.D. Suenram, A.C. Legon, *J. Chem. Phys.* 111 (1999) 5764.
- [3] J. Castillo-Chara, R.R. Lucchese, J.W. Bevan, *J. Chem. Phys.* 115 (2001) 899.
- [4] A. McIntosh, P. Lin, R.R. Lucchese, J.W. Bevan, D.J. Brugh, R.D. Suenram, *Chem. Phys. Lett.* 331 (2000) 95.
- [5] P. Lin, W. Jabs, R.R. Lucchese, J.W. Bevan, D.J. Brugh, R.D. Suenram, *Chem. Phys. Lett.* 356 (2002) 101.
- [6] M.R. Keenan, E.J. Campbell, T.J. Balle, L.W. Buxton, T.K. Minton, P.D. Soper, W.H. Flygare, *J. Chem. Phys.* 72 (1980) 3070.
- [7] J.M. Hutson, A.E. Barton, P.R.R. Langridge-Smith, B.J. Howard, *Chem. Phys. Lett.* 73 (1980) 218.
- [8] B.J. Howard, *Faraday Discuss. Chem. Soc.* 71 (1981) 23.
- [9] K.C. Jackson, P.R.R. Langridge-Smith, B.J. Howard, *Mol. Phys.* 39 (1980) 817.
- [10] W.G. Read, E.J. Campbell, *J. Chem. Phys.* 79 (1983) 1669.
- [11] D.W. Firth, M.A. Dvorak, S.W. Reeve, R.S. Ford, K.R. Leopold, *Chem. Phys. Lett.* 168 (1990) 161.
- [12] J. Han, A.L. McIntosh, Z. Wang, R.R. Lucchese, J.W. Bevan, *Chem. Phys. Lett.* 265 (1997) 209.
- [13] J. Andzelm, S. Huzinaga, M. Klobukowski, E. Radzio, *Chem. Phys.* 100 (1985) 1.
- [14] J.M. Hutson, *J. Chem. Phys.* 91 (1989) 4455.
- [15] S.P. Belov, B.A. McElmurry, W. Jabs, R.R. Lucchese, J.W. Bevan, I. Leonov (to be published).
- [16] K.A. Walker, A.R.W. McKellar, *J. Mol. Spectrosc.* 205 (2001) 331.
- [17] D.G. Melnik, S. Gopalakrishnan, T.A. Miller, F.C. De Lucia, S. Belov, *J. Chem. Phys.* 114 (2001) 6100.
- [18] I. Morino, M. Fabian, H. Takeo, K.M.T. Yamada, *J. Mol. Spectrosc.* 185 (1997) 142.
- [19] F.A. Van Dijk, A. Dymanus, *Chem. Phys.* 6 (1974) 474.
- [20] F.C. De Lucia, P. Helminger, W. Gordy, *Phys. Rev. A* 3 (1971) 1849.
- [21] C.H. Townes, A.L. Schawlow, *Microwave Spectroscopy*, McGraw-Hill, New York, 1955.
- [22] J. Castillo-Chara, J.W. Bevan, R.R. Lucchese, *Comput. Phys. Comm.* 145 (2002) 48.