

See discussions, stats, and author profiles for this publication at:  
<https://www.researchgate.net/publication/244130464>

# A REMPI study of styrene and trans- $\beta$ -methylstyrene clusters in a supersonic jet

ARTICLE *in* CHEMICAL PHYSICS LETTERS · APRIL 1995

Impact Factor: 1.9 · DOI: 10.1016/0009-2614(95)00217-R

---

CITATIONS

16

---

READS

11

2 AUTHORS, INCLUDING:



Shai Kendler

Israel Institute of Biological Research

19 PUBLICATIONS 203 CITATIONS

SEE PROFILE

# A REMPI study of styrene and trans- $\beta$ -methylstyrene clusters in a supersonic jet

S. Kendler, Y. Haas

*Department of Physical Chemistry and the Farkas Center for Light-Induced Processes, The Hebrew University of Jerusalem, Jerusalem 91904, Israel*

Received 9 January 1995; in final form 7 February 1995

---

## Abstract

Clusters of styrene and  $\beta$ -methylstyrene (BMS) with argon and of styrene with molecular nitrogen were prepared in a supersonic jet. The vibrational frequencies of the solvated styrenes in  $S_1$  are very similar to that of the bare molecule, but some small, non-negligible differences are noted. A correlation between the observed solvent shift and the changes of the vibrational frequencies upon  $S_0 \rightarrow S_1$  excitation in the bare molecule is found and discussed. In addition, the binding energies and some van der Waals frequencies are estimated from the data.

---

## 1. Introduction

The  $S_0 \leftrightarrow S_1$  ( $(X(^1A') \leftrightarrow \tilde{A} (^1A'))$ ) transition of styrene (STY) [1–5] and styrene derivatives [6–14] has been extensively studied experimentally, and it has been established that the  $S_1$  state is planar. The structure of the ground state was more difficult to establish, since the torsional potential was found to be extremely anharmonic [1,3]. It is generally believed now that styrene is essentially planar in the ground state also, but the potential energy surface is almost flat when the torsional angle is varied between  $-20^\circ$  and  $+20^\circ$ . In a recent study, Sinclair et al. [14] found that in the case of trans- $\beta$ -methylstyrene (BMS) the equilibrium structure is actually non-planar, the ground state potential having a small maximum at the planar conformation. Theoretical studies, using semi-empirical [15,16] or ab initio [17,18] methods, generally confirmed these findings, although in the case of styrene itself, a small local

maximum is found in these calculations for a vanishing torsional angle. The magnitude of this maximum ( $\approx 20 \text{ cm}^{-1}$ ) is so small that this result may be due to a computational artifact.

We have recently completed an ab initio study of STY and BMS in their lowest three singlet states [19], in which all the vibrational normal modes of these states were computed. Agreement with experiment was generally very good, and the previous experimental assignments were largely confirmed. For some of the lowest frequency out-of-plane modes an alternative assignment was offered, but the calculation of these very ‘soft’ and anharmonic vibrational modes may require a much more extensive calculation than the RHF/4-31G one used in Ref. [19]. Thus, pending further experimental results, the classic work of Hollas and co-workers [1,3] is largely acceptable.

The computed correlation between the normal modes in  $S_0$  and  $S_1$  revealed an interesting pattern:

most of the frequencies were smaller in the excited state than in the ground state. This trend was particularly conspicuous for the ring out-of-plane modes, for which a frequency decrease by 20%–40% was common. For in-plane modes the change was more modest, the decrease never exceeding 10%. Some exceptions were found, the most prominent being the in-plane  $\nu_{17}$  mode (analogous to  $\nu_{14}$  in benzene, o-type in Whiffen's notation for substituted benzenes [20]), which showed a 30% frequency *increase* upon electronic excitation. The low frequency modes (in-plane and out-of-plane) exhibited only small changes, and the frequency of the torsional mode ( $\nu_{42}$  in STY), was found to increase a bit. The frequency decrease upon electronic excitation was found to be due mainly to the decrease in force constant; since bonding is usually weakened upon electronic excitation, this is indeed an expected trend. The larger frequency decrease in the out-of-plane modes was ascribed to the 'dilution' of the  $\pi$ -electron density which results in a smaller restoring force for such motion (see Fig. 10 in Ref. [19]).

Clusters of styrene and styrene derivatives in supersonic jets were studied by several authors [13,21–24]. The binding energies of some clusters in the ground and excited states were established for some pairs, such as STY–Ar and 4-fluorostyrene–Ar. In this work, we report a REMPI study of the STY–Ar, STY–N<sub>2</sub> and BMS–Ar clusters, for which we determined the dissociation energies and some van der Waals vibrational frequencies. These data are compared with a calculation based on an empirical potential. In addition, the *internal* frequencies of some styrene vibrational modes are found to change in  $S_1$  upon complexation. These changes are small, but way beyond experimental error, and appear to be correlated qualitatively with the calculated effects on these modes upon  $S_0 \rightarrow S_1$  excitation, reported in Ref. [19].

## 2. Experimental

A conventional pulsed supersonic beam apparatus was constructed for this work. Clusters of styrene and BMS with argon or nitrogen were prepared by expanding a mixture containing the vapor of the organic molecule (in equilibrium with the liquid

which was held at room temperature) with the appropriate gas through a small nozzle into a high vacuum chamber. For argon clusters the carrier gas was pure argon, at a pressure of 2.5 and 1.2 atm for STY and BMS, respectively. Nitrogen clusters were prepared by adding helium to 200 Torr N<sub>2</sub> up to a total pressure of 5.5 atm and flowing the mixtures over the liquid styrene and into the nozzle. The 0.45 mm, 30° conical nozzle was mounted in an electromagnetic operated pulsed valve that was run at 10 Hz, with a typical opening time of 150  $\mu$ s [25].

The expansion chamber was pumped by a 1200 l/s (Varian) diffusion pump, achieving a background pressure of  $\approx 10^{-6}$  mbar, and working pressure of  $\approx 5 \times 10^{-5}$  mbar when the nozzle was operated with a backing pressure of 5.5 atm. The resulting jet was skimmed 4 cm downstream by a 2 mm diameter electro-deposited nickel skimmer (Beam Dynamics). The ion source of a time-of-flight mass spectrometer (TOFMS) was mounted in a differentially pumped stainless steel chamber on the other side of the skimmer, which was evacuated by a 120 l/s turbomolecular pump (alcatel). The background pressure in this chamber was  $10^{-7}$  mbar, and it rose to  $10^{-6}$  when the nozzle was operated. The molecular beam was crossed by a tunable dye laser beam 23 cm downstream from the skimmer, in the center of the ion source. The TOFMS was a Wiley–McLaren type [26] with a two stage acceleration source, and a 135 cm long field free drift tube, which was pumped by a 80 l/s turbomolecular pump (Alcatel). Acceleration voltages were typically 215 and 2870 V/cm in the first and second stages, respectively. A Daley type ion detector was similar in design to that described in Ref. [25]: the ions were accelerated onto a polished aluminum curved plate with a –20 kV potential, and the generated electrons were directed to a plastic scintillator. The ions were allowed to pass through a 10 mm aperture placed 6 cm before the detector, improving the mass resolution, which was about  $m/\Delta m = 630$ . The improvement appears to arise from the fact that ions travelling with curved trajectories, and therefore arriving at a slight delay with respect to those travelling near the axis are prevented from reaching the detector, as a computer simulation shows. In addition, the aperture limits the effective active area of the aluminum plate, which is mounted at a strongly oblique angle

with respect to the incoming ions. Light emitted from the scintillator was detected by a nearby photomultiplier tube (Hamamatsu R1635-02) placed outside the vacuum chamber. The PM signal, amplified by a 150 MHz pulse amplifier (Keithley 107) was fed into a digital oscilloscope (Tektronix 2440). Signal averaging and analysis was made by an on-line personal computer that also controlled the experiment.

Ionization was initiated by a pulsed doubled dye laser pumped by an excimer laser (Lambda Physik DL3002 and EMGMSC150, respectively); its beam was mildly focused into the cell by a 50 cm lens. Typical laser pulse energy in the ion source was 10  $\mu\text{J}$  with a 15 ns pulse width and 0.4  $\text{cm}^{-1}$  resolution.

### 3. Results

#### 3.1. Experimental results

When STY or BMS expanded in pure helium were irradiated at or slightly above the origin of their respective  $S_0 \rightarrow S_1$  transitions, the mass-resolved REMPI spectrum consisted mainly the parent ion peak; very little fragment ions were observed. Expansion in argon and tuning the laser to the red of the parent molecule 0, 0 band, led to the appearance of new mass peaks, the most prominent of them corresponding to the 1:1 cluster ion styrene–argon ( $m/z = 144$  and 158 for STY and BMS, respectively). The origins of the transition due to the 1:1 STY–Ar and BMS–Ar were red-shifted from the origins of the bare molecules by 30.6 and 35.5  $\text{cm}^{-1}$  for STY and BMS, respectively. This shift, and the whole excitation spectrum of styrene–argon was found to be similar to that published in Ref. [21], and is shown in Fig. 1 together with the corresponding spectra of STY– $\text{N}_2$  and BMS–Ar. Tables 1 and 2 summarize the frequencies and relative intensities of the main bands in the excitation spectrum of the STY–Ar and BMS–Ar clusters. The low frequency portion of the REMPI excitation spectrum of these species is also shown at an expanded scale in Fig. 1. The STY– $\text{N}_2$  spectrum, whose origin lies at  $-25.5 \text{ cm}^{-1}$  from the STY origin, is seen to be consider-

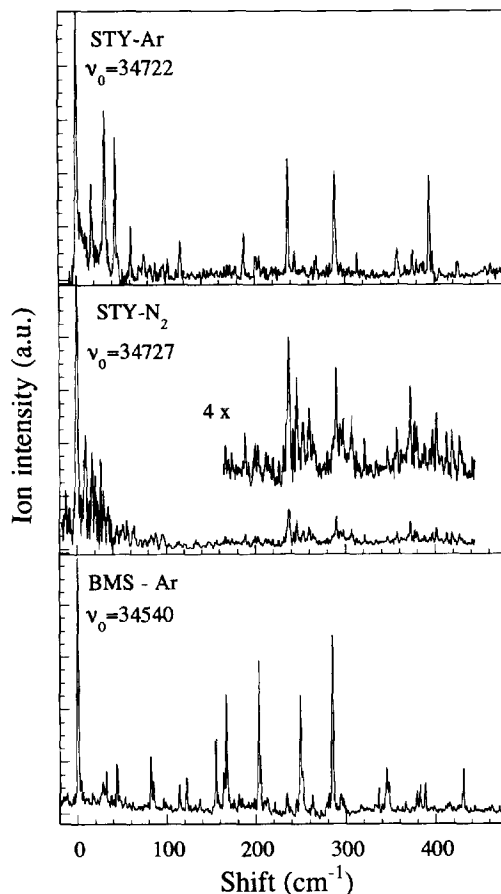


Fig. 1. The REMPI excitation spectrum of the clusters STY–Ar, STY– $\text{N}_2$  and BMS–Ar. The shift is with respect to the origins of the respective clusters, also shown in the figure. The inset in the middle frame shows the STY– $\text{N}_2$  spectrum at an expanded scale. Note that the  $\Delta E = 394 \text{ cm}^{-1}$  feature, strong in the STY–Ar case, is quite weak in the STY– $\text{N}_2$  spectrum.

ably more congested than the spectra due to argon clusters.

Many of the vibrational bands appearing in the styrenes–argon 1:1 cluster MPI excitation spectrum could be correlated with corresponding peaks in the bare molecule spectrum. The excitation spectra could be observed by monitoring either the adduct ion itself, or the adduct minus solvent molecule (namely, the bare styrene molecular ion). As discussed below, the observation of bare molecular ions even when the adduct was excited at the 0, 0 band of the cluster  $S_0 \rightarrow S_1$  transition, is due to the fact that the energy of two photons suffices not only to ionize the cluster,

but also to dissociate the nascent cluster ion. Fig. 2 shows a plot of the ratio of the parent cluster ion signal intensity to the bare molecule ion signal intensity as a function of excess energy,  $\Delta E$ , over the 0, 0 band for the BMS–Ar 1:1 cluster. A sharp decrease in this ratio, observed at a certain excess energy ( $\approx 400 \text{ cm}^{-1}$ ), is ascribed to the onset of the dissociation of the *neutral* cluster in  $S_1$  (see Section 4.1). The cluster bond dissociation energy,  $D_{\text{ES}}$ , in the excited state can therefore be estimated from this plot. In addition,  $E_{\text{GS}}$  of the neutral cluster in the ground electronic state is obtained from the measured shift of the cluster 0, 0 band from the parent one, using the method previously employed for styrene–argon [21].

The excitation spectra of STY– $\text{N}_2$  clusters are complicated by a rich vibrational structure accompanying each band, presumably arising from low frequency van der Waals modes. Nevertheless, the strong transitions at the origin, and at  $\Delta E = 237$ , 288.3 and  $375.4 \text{ cm}^{-1}$  can be detected and  $D_{\text{ES}}(\text{STY–N}_2)$  can be estimated from the fact that the strong feature expected at  $\Delta E = 394 \text{ cm}^{-1}$  is actually quite weak. A value of  $\Delta E = 375 \pm 25 \text{ cm}^{-1}$  is estimated from the data. The many weak resonance bands observed in the 375–400  $\text{cm}^{-1}$  range may arise from molecules excited just beyond the dissociation energy. Their vibrational predissociation lifetimes are relatively long so that a certain fraction is ionized before fragmentation takes place.

Table 1  
Vibrational levels observed in the  $S_0 \rightarrow S_1$  transition of styrene and styrene–Ar 1:1 adducts

Styrene			Styrene–argon			$\Delta\Delta E$ (cm <sup>−1</sup> ) <sup>b</sup>	
$\Delta E$ (cm <sup>−1</sup> ) <sup>a</sup>	assignment		rel. intensity	$\Delta E$ (cm <sup>−1</sup> )	assignment		rel. intensity
	Ref. [19]	Ref. [5]					
0.0	origin		100.0	0.0	origin	100 <sup>c</sup>	
				17.1	$\nu_1$ <sup>d</sup>	22	
				32.4	$\nu_2$ <sup>d</sup>	47	
				44.2	$\nu_3$ <sup>d</sup>	32	
				61.2	$2 \times \nu_2$	10	
				100.7	?	14	
193.2	42 <sub>0</sub> <sup>6</sup>	41 <sub>0</sub> <sup>2</sup>	1.1	188.0	42 <sub>0</sub> <sup>6</sup>	16	−5.2
				203.0	42 <sub>0</sub> <sup>6</sup> + $\nu_1$	9	
237.2	29 <sub>0</sub> <sup>1</sup>	29 <sub>0</sub> <sup>1</sup>	10.5	237.3	29 <sub>0</sub> <sup>1</sup>	41	0.1
				244.5	?	10	
				269.4	29 <sub>0</sub> <sup>1</sup> + $\nu_2$	16	
282.4	40 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup>	41 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup>	7.8	288.3	40 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup>	39	5.9
				313.5	29 <sub>0</sub> <sup>1</sup> + $\nu_2$ + $\nu_3$	8	
349.1	39 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup> or 40 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>3</sup>	40 <sub>0</sub> <sup>1</sup> 41 <sub>0</sub> <sup>1</sup>	7.0	358.0	39 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup> or 40 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>3</sup>	10	8.9
371.0	41 <sub>0</sub> <sup>2</sup>	42 <sub>0</sub> <sup>2</sup>	2.0	375.4	41 <sub>0</sub> <sup>2</sup>	9	4.4
394.5	28 <sub>0</sub> <sup>1</sup>	28 <sub>0</sub> <sup>1</sup>	15.5	394.0	28 <sub>0</sub> <sup>1</sup>	38	−0.5
437.1	41 <sub>0</sub> <sup>2</sup> 42 <sub>0</sub> <sup>2</sup> or 40 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>3</sup>	27 <sub>0</sub> <sup>1</sup>	2.3	425.6	28 <sub>0</sub> <sup>1</sup> + $\nu_2$	13	

<sup>a</sup>  $\Delta E$  is the energy of the observed vibronic band with respect to the 0, 0 transition.

<sup>b</sup>  $\Delta\Delta E = \Delta E_{\text{STY–Ar}} - \Delta E_{\text{STY}}$ .

<sup>c</sup> This band was saturated, in order to obtain a better signal upon excitation of the weaker vibronic bands.

<sup>d</sup>  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  are the three frequencies associated with the van der Waals bond between argon and styrene.

The results for the three clusters in the ground and first electronic excited state are collected in Table 3. The table includes also the results of empirical potential calculations described in Section 3.2. Fig. 3 shows schematically the energy level diagram for the STY–Ar cluster, for which the dissociation energy of the cluster ion was also measured. A similar diagram applies for the STY–N<sub>2</sub> and BMS–Ar clusters; it is noted that knowledge of the dissociation

energy of the cluster ion is not required for the determination of the neutral cluster dissociation energy.

### 3.2. Potential surfaces calculations

An approximate energy surface was calculated for the clusters by using empirically based potential functions generated from pairwise added atomic

Table 2  
The vibrational structure of the S<sub>0</sub> → S<sub>1</sub> of BMS and BMS–Ar 1:1 adducts

BMS			BMS–Ar			$\Delta\Delta E$ (cm <sup>-1</sup> ) <sup>b</sup>
$\Delta E$ (cm <sup>-1</sup> ) <sup>a</sup>	assignment Ref. [36]	rel. intensity	$\Delta E$ (cm <sup>-1</sup> ) <sup>a</sup>	assignment	rel. intensity	
0.0	origin	100.0	0.0	origin	100 <sup>c</sup>	
			16.6	$\nu_1$ <sup>d</sup>	7	
			28.6	$2\nu_1(?)$	12	
			32.0	$\nu_2$ <sup>d</sup>	16	
			43.0	$\nu_3$ <sup>d</sup>	19	
81.3	?	1.2	82.0	?	22	0.7
			114.2	$34_0^1$ (BMS–Ar <sub>2</sub> ) <sup>e</sup>	11	
			122.0	?	14	
156.3	$34_0^1$	15.6	155.1	$34_0^1$	26	-1.2
			166.8	$50_0^2$ (BMS–Ar <sub>2</sub> ) <sup>e</sup>	42	
198.6	$50_0^2$	13.1	203.2	$50_0^2$	57	4.6
			235.0	$50_0^2 + \nu_2$	10	
244.5	$50_0^2 51_0^2$	13.3	249.7	$50_0^2 51_0^2$	45	5.2
			262.8	?	6	
284.0	$49_0^1 50_0^1$	13.5	284.0	$49_0^1 50_0^1$	68	0
337.0	$33_0^1$	9.3	336.0	$33_0^1$	10	-1.0
			345.0	$32_0^1$ (BMS–Ar <sub>2</sub> ) <sup>e</sup>	17	
378.4	$49_0^1 50_0^1 51_0^4$	4.7	378.8	$49_0^1 50_0^1 51_0^4$	9	0.4
			381.5	?		
388.3	$32_0^1$	12.4	388.2	$32_0^1$	12	-0.1
426.2	$48_0^2$	6.7	430.3	$48_0^2$	17	4.1

<sup>a</sup>  $\Delta E$  is the energy of the observed vibronic band with respect to the 0, 0 transition.

<sup>b</sup>  $\Delta\Delta E = \Delta E_{\text{BMS–Ar}} - \Delta E_{\text{BMS}}$ .

<sup>c</sup> This band was saturated, in order to obtain a better signal upon excitation of the weaker vibronic bands.

<sup>d</sup>  $\nu_1$ ,  $\nu_2$  and  $\nu_3$  are the three frequencies associated with the van der Waals bond between argon and BMS.

<sup>e</sup> Bands assigned to absorption by the trimer BMS–Ar<sub>2</sub>.

Lennard–Jones (LJ) 12–6 potentials [27–29]. Three different potentials were used, whose parameters are listed in Table 4. When the potential parameters for the methyl H and C atoms given in Ref. [27] were used, agreement with the experimental dissociation energies is not so good. These parameters were found to lead to good agreement for the methyl group in *o*-xylene, i.e. for the situation in which two neighboring methyl groups are attached directly to the aromatic ring. It appears that when a single methyl group is attached to a vinyl group, rather different LJ parameters are needed. Adopting the parameters for the methyl group from Ref. [28] not only improved the calculated results for the BMS–Ar complex but also reproduced the difference between STY–Ar and BMS–Ar, induced mainly because of the methyl group. Treating this group as a single atom, which makes the calculation somewhat faster and simpler, turns out to yield satisfactory results. Parameters for the interaction of the excited state with argon were taken from Ref. [27], modified for the methyl group as above. For nitrogen, the parameters were calculated using the method of Ref. [29]. For the  $S_1$  excited state, the same H–N interaction parameters as in  $S_0$  were used, while the C–N ones were modified as shown in Table 4.

The global minimum on the potential surface was located by applying the simulated annealing method

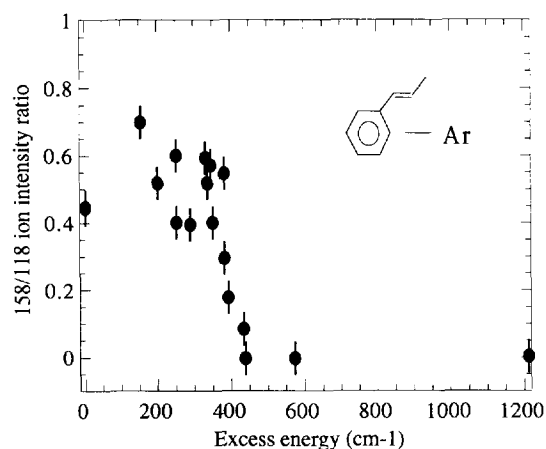


Fig. 2. The ratio of the parent ion signal intensity ( $I_{\text{BMS-Ar}^+}$ ) to that of the daughter ion signal intensity ( $I_{\text{BMS}^+}$ ), both measured for excitation of the same cluster band, as a function of excess energy  $\Delta E$  with respect to the origin. The cluster dissociation energy is determined from the data to be  $430^{+10}_{-30}$   $\text{cm}^{-1}$ .

Table 3

Some calculated properties of styrene and BMS adducts

	Exp.	Pot. I	Pot. II	Pot. III
STY–Ar( $S_0$ )				
$D_{\text{GS}}$ ( $\text{cm}^{-1}$ )	385	353	394	–
$R_z$ ( $\text{\AA}$ )		3.54	3.48	
$\nu_{\text{STR}}$ ( $\text{cm}^{-1}$ )		40.4	38.2	–
STY–Ar( $S_1$ )				
$D_{\text{ES}}$ ( $\text{cm}^{-1}$ )	416	397	–	–
$R_z$ ( $\text{\AA}$ )		3.47	–	–
$\nu_{\text{STR}}$ ( $\text{cm}^{-1}$ )	44.2	39.4	–	
BMS–Ar( $S_0$ )				
$D_{\text{GS}}$ ( $\text{cm}^{-1}$ )	395	356	432	395
$R_z$ ( $\text{\AA}$ )		3.54	3.42	3.46
$\nu_{\text{STR}}$ ( $\text{cm}^{-1}$ )	–	38.7	38.7	39.9
BMS–Ar( $S_1$ )				
$D_{\text{ES}}$ ( $\text{cm}^{-1}$ )	430	400?		434
$R_z$ ( $\text{\AA}$ )		3.47	–	3.41
$\nu_{\text{STR}}$ ( $\text{cm}^{-1}$ )	43.0	39.0	–	40.0
STY–N <sub>2</sub> ( $S_0$ )				
$D_{\text{GS}}$ ( $\text{cm}^{-1}$ )	350	364	–	–
$R_z$ ( $\text{\AA}$ )		3.51	–	–
STY–N <sub>2</sub> ( $S_1$ )				
$D_{\text{ES}}$ ( $\text{cm}^{-1}$ )	375	386	–	–
$R_z$ ( $\text{\AA}$ )		3.41	–	–

See Table 4 for the parameters used in the calculations with the three potential functions.  $D_{\text{GS}}$  is the bond dissociation of the styrene–argon adduct in  $S_0$ .  $D_{\text{ES}}$  is the bond dissociation of the styrene–argon adduct in  $S_1$ .  $R_z$  is the vertical displacement of the argon atom from the aromatic ring.  $\nu_{\text{STR}}$  is the energy separation between the  $v=1$  and  $v=0$  levels of the styrene–argon stretching frequency.

[30]. The resulting potential surfaces for styrene–argon and BMS–argon are shown in Fig. 4 as contour plots, along with a schematic representation of the structures. Experimental values for the geometry of styrene–argon 1:1 adducts are not available; the vertical calculated displacement of the argon atom from the aromatic ring,  $R_z$ , 3.48 and 3.42  $\text{\AA}$  for STY and BMS, respectively, is close to the measured value for the benzene–argon adduct, 3.50  $\text{\AA}$  [31]. For  $S_1$ , a small decrease in  $R_z$  is calculated, in agreement with observed decrease of 45 m $\text{\AA}$  observed for the benzene–Ar cluster [32].

The van der Waals stretching frequencies were estimated by assuming that the mode can be approximated as the relative motion of the two constituents

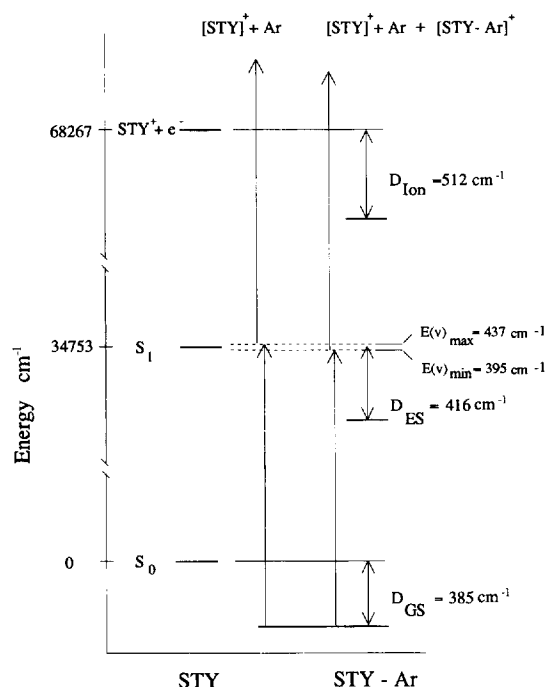


Fig. 3. A partial energy level diagram of the neutral and ionic STY-Ar 1:1 adducts, showing the dissociation energies of the ground state adduct,  $D_{GS}$ , of the excited state one,  $D_{ES}$ , and of the ion,  $D_{ion}$ .  $E(v)_{min}$  is the energy of the highest internal vibrational levels of styrene in the adduct for which the parent ion signal is observable.  $E(v)_{max}$  is the energy of the next vibrational level; the energy difference between these levels is the main source of the uncertainty in determining  $D_{ES}$ , and hence  $D_{GS}$ . Data for the ionic adduct are from Ref. [22].

of the cluster along the line connecting their centers of mass, in the following way: The  $x$  and  $y$  coordinates of the minimum energy structure were kept constant, while the potential curve along the  $z$  coordinate was fitted to a Morse potential of the form

$$V = D[1 - \exp(-\beta q)]^2, \quad (1)$$

in which the relations  $\beta = \omega_e(2\pi^2c\mu/Dh)^{1/2}$  and  $q = R - R_e$  are used.  $D$  is the dissociation energy,  $R$  the distance between the center of mass of the styrene and the center of mass of the argon (or nitrogen molecule),  $R_e$  the equilibrium value of  $R$ ,  $h$  is Planck's constant,  $\mu$  the reduced mass of the adduct with respect to the stretching mode,  $\omega_e$  is the vibrational harmonic constant and  $\omega_e x_e$ , the anharmonic constant is obtained from the relation  $\omega_e x_e = \omega_e^2/4D_e$ . The frequencies of the calculated vibrational  $\Delta v = 1$  transitions are compared in Table 3 with observed values.

#### 4. Discussion

In this work the dissociation energies for some styrene-based 1:1 adducts in the ground and first electronically excited state,  $S_1$ , were measured as well as the changes in the frequencies of internal vibronic bands in  $S_1$  due to the adduct formation. The discussion will begin by considering the energet-

Table 4  
Lennard-Jones potential parameters used in the cluster energy calculations

	$S_0$		$S_1$	
	$\epsilon$ (cm <sup>-1</sup> )	$\sigma$ (Å)	$\epsilon$ (cm <sup>-1</sup> )	$\sigma$ (Å)
potential I				
C-Ar <sup>a</sup>	35.030	3.480	40.590	3.410
H-Ar <sup>a</sup>	33.014	3.208	33.014	3.208
C-N <sup>b</sup>	21.300	3.390	22.710 <sup>c</sup>	3.320 <sup>c</sup>
H-N <sup>b</sup>	14.100	3.040	14.100 <sup>c</sup>	30.400 <sup>c</sup>
potential II <sup>d</sup>				
C-Ar	40.200	3.420		
H-Ar	33.000	3.210		
CH <sub>3</sub> -Ar	93.000	3.600		
potential III				
as in potential I, except that the methyl group was treated as a single entity with the following parameters:				
CH <sub>3</sub> -Ar <sup>d</sup>	93.000	3.600	93.000	3.600

<sup>a</sup> Ref. [27]. <sup>b</sup> Calculated from the data of Ref. [29].

<sup>c</sup> This work. <sup>d</sup> Ref. [28].



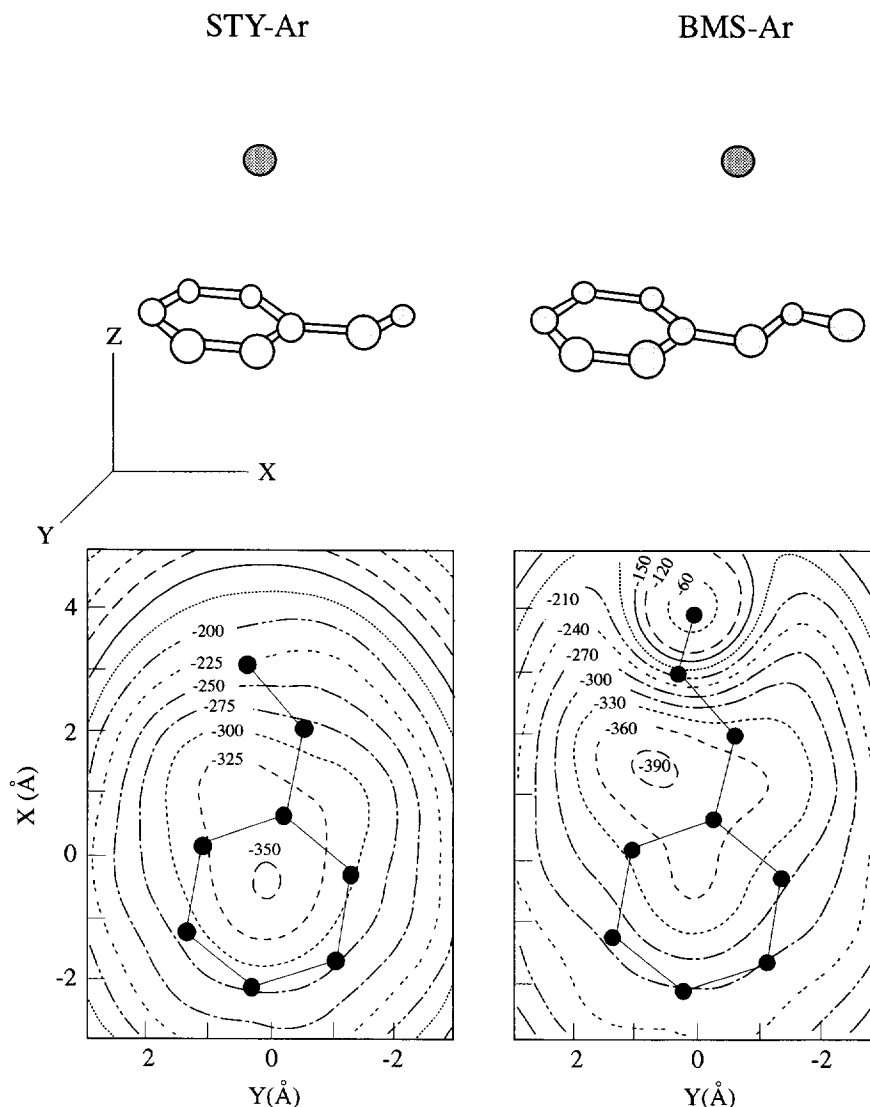


Fig. 4. Cartoons of the structures of the STY-Ar and BMS-Ar 1:1 adducts, and contour plots of the calculated potential surfaces. The figure shows the results obtained with potential III (see Table 4).

ics and structure of the adducts, and then offer a rationalization of the vibronic shifts.

#### 4.1. Styrene adducts energetics and dynamics

The binding energies of the STY-Ar 1:1 adduct in  $S_0$  and  $S_1$  have been measured in Ref. [21] to be  $396$  and  $426\text{ cm}^{-1}$ , respectively. Our values of  $385 \pm 20$  and  $416 \pm 20$  are in good agreement with these

data. In both cases the results are based on the change in the parent ion signal's intensity as a function of excess energy in  $S_1$ , as shown in Fig. 2. In a one-color, two-photon REMPI experiment, the decrease could be due to a dissociation of either the neutral or ion cluster. In the present case, however, evidence for the neutral channel appears to be convincing, as discussed below using the STY-Ar adduct as an example. It was chosen since detailed numeri-

cal data for the ion cluster are available for this system, but the arguments can be applied to STY–N<sub>2</sub> and BMS–Ar as well.

The ionization potential of the STY–Ar 1:1 adduct and the dissociation energy of the cluster ion are 68151 and 512 cm<sup>-1</sup>, respectively [22]. The combined energy of two photons at the resonance energy of the 0, 0 transition of the adduct is 69442 cm<sup>-1</sup>; it suffices to ionize the cluster, and if all available energy remains in the ion (i.e. for zero energy electrons), also to dissociate the ion. Thus the appearance of the molecular ion (STY<sup>+</sup>) upon excitation at this frequency is accounted for. However, since in many ionization events a large fraction of the energy goes to the electron, many cluster ions are formed with little internal energy and do not dissociate while in the acceleration zone of the TOFMS (typically 1.5 μs in these experiments).

The relatively small size of the cluster results in a large unimolecular rate constant for its dissociation, even at very modest excess energies. Assuming a rapid intramolecular redistribution of energy in the cluster (between intermolecular and van der Waals modes alike), we made an RRKM calculation of the unimolecular rate constant. It was found that with an excess energy of 50 cm<sup>-1</sup>, the adduct would dissociate with a rate constant of  $3.6 \times 10^{10} \text{ s}^{-1}$  and even with an excess energy of only 10 cm<sup>-1</sup>, the unimolecular half life is about 0.5 ns. This means that on the time scale of the experiment (namely residence time in the ion source), the cluster dissociates promptly as soon as it attains enough internal energy. This reasoning holds for both the ion and the neutral clusters. As Fig. 2 shows for the BMS–Ar cluster, the  $I_{(\text{BMS-Ar})^+}/I_{\text{BMS}^+}$  ratio is approximately constant at  $0.55 \pm 0.15$  up to  $\Delta E \approx 400 \text{ cm}^{-1}$ , and then drops to zero over a 50 cm<sup>-1</sup> span. The small added energy in the ion is not likely to change suddenly the energy distribution between the electron and the ion, leading to complete dissociation of all ions. The most likely explanation is the onset of dissociation of the electronically excited neutral cluster, which, as soon as its energy exceeds the binding energy, would immediately dissociate.

The rapid dissociation of the molecular adduct as its internal energy exceeds the dissociation energy, and the validity of the RRKM calculation, are based on the assumption of rapid intramolecular vibration

redistribution (IVR) in the cluster, involving both intra-molecular vibrations, and van der Waals ones. This is not necessarily the general case, and indeed benzene–argon clusters [33] are known to fluoresce on excitation to the 6<sup>1</sup> vibration of S<sub>1</sub>, which lies at  $\Delta E = 521 \text{ cm}^{-1}$ . Furthermore, high resolution spectra of this cluster [32] and of the benzene–N<sub>2</sub> cluster [34] have been obtained at this excitation energy, indicating a stable species on the rotational time scale. This energy exceeds the binding energy ( $< 340 \text{ cm}^{-1}$  according to Ref. [15],  $408 \text{ cm}^{-1}$  by Ref. [31]). In benzene, there are no low-lying intramolecular vibrations, and it appears that the coupling to the van der Waals ones is slow enough to permit observation of fluorescence. In the styrenes, the lowest lying out-of plane mode is close enough in energy to the intermolecular stretching vibration, making energy redistribution among *all* modes of the adduct rapid on the time scale of the fluorescence.

The rather dense vibrational structure of the absorption spectrum of the styrenes provides a unique opportunity to measure the binding energy of van der Waals adducts accurately. Furthermore, inspection of Fig. 2 shows that several data points are observable in the  $\approx 100 \text{ cm}^{-1}$  interval between the initial value of  $I_{(\text{BMS-Ar})^+}/I_{\text{BMS}^+}$  ( $\approx 0.55$ ) and the final disappearance of the parent signal. This is a possible indication of slow IVR when the excess energy in S<sub>1</sub> is very small.

#### 4.2. Solvation effects on the internal vibrations

Following the detailed theoretical analysis of the vibrational structure of styrene and BMS [19], we took considerable care to measure accurately the vibrational structure of the S<sub>0</sub> → S<sub>1</sub> transition of the clusters studied in this work. The vibrational frequencies we observed for the STY–Ar 1:1 cluster van der Waals vibrational modes are in very good agreement with those of Ref. [23] and in fair agreement with those of Ref. [21]. As for other systems, the crude model using pairwise interactions appears to account for the results reasonably well. We were, however, particularly interested in solvent shift effects on the *internal* frequencies ( $\nu_{\text{int}}$ ) of the styrenes. Comparison of the internal frequencies of styrene listed for the cluster in Table 1, with the values given in Ref. [21] for these frequencies shows that the

agreement is not very good. However, the values found by us for the bare molecules are in excellent agreement with literature data for styrene and BMS [5,14]. The small, but clearly measurable changes in  $\nu_{\text{int}}$  for some vibronic modes of the  $S_1$  state taking place in the molecule upon solvation by an argon atom (cf. the last columns in Tables 1 and 2) is therefore considered to be genuine.

Inspection of these tables reveals an interesting pattern in  $\Delta\Delta E$ : For all in-plane modes in both styrene and BMS, the solvent shift is small, being in fact within the error limit. On the other hand, all the larger shifts ( $\Delta\Delta E > 4 \text{ cm}^{-1}$ ) are due to out-of-plane modes. In Ref. [19] we discussed the correlation between the vibrational modes of the  $S_0$  and  $S_1$  states, as briefly summarized in Section 1. Table 5 summarizes the observed  $\Delta\Delta E$  values found for the STY–Ar and BMS–Ar clusters, and lists also the changes in the frequencies of the modes ( $\Delta\nu(S_0-S_1)$ ) of the bare molecules upon electronic excitation. A

qualitative reverse correlation is immediately observed: out-of-plane modes for which  $\Delta\nu(S_0-S_1)$  is negative, show a positive  $\Delta\Delta E$  while transitions in which modes for which a positive  $\Delta\nu(S_0-S_1)$  is calculated are involved, show a negligible or even a negative  $\Delta\Delta E$ . Examples for the latter are the  $\Delta E = 284$  and  $378 \text{ cm}^{-1}$  bands of BMS, in which  $\nu_{49}$  is involved. This mode is one of the few out-of-plane ones, for which  $\Delta\nu(S_0-S_1)$  is positive.

A rationalization for this correlation may be discussed in term of the reasons for the generally observed negative value of  $\Delta\nu(S_0-S_1)$ . It is due to the ‘softening’ of the out-of-plane restoring force by the  $\pi$ -electron cloud, which is ‘diluted’ by electronic excitation [19]. Complexation with an argon atom, whose equilibrium position is shown in Fig. 4, namely, above the molecular plane, is expected to have a localization effect on the  $\pi$ -electrons, leading to an increase in the restoring force constant. For modes whose force constant increased upon excita-

Table 5

A summary of the changes observed in the intramolecular vibrations of styrene and BMS in  $S_1$  upon complexation with argon (frequencies in  $\text{cm}^{-1}$ )

Styrene						BMS					
Assign. <sup>a</sup>	bare molecule <sup>b</sup>	cluster <sup>b</sup>	$\Delta\Delta E$ <sup>c</sup>	$\Delta\nu(S_0-S_1)$ <sup>d</sup>		Assign. <sup>e</sup>	bare molecule <sup>b</sup>	cluster <sup>b</sup>	$\Delta\Delta E$ <sup>f</sup>	$\Delta\nu(S_0-S_1)$ <sup>d</sup>	
				exp.	calc.					exp.	calc.
in-plane vibrations											
29 <sub>0</sub> <sup>1</sup>	237.2	237.3	0.1	0	9	34 <sub>0</sub> <sup>1</sup>	156.3	155.1	−1.2	13	1
28 <sub>0</sub> <sup>1</sup>	394.5	394.0	−0.5	43	15	33 <sub>0</sub> <sup>1</sup>	337.0	336.0	−1.0	−5	0
						32 <sub>0</sub> <sup>1</sup>	388.3	388.2	−0.1	0	−21
out-of-plane vibrations											
42 <sub>0</sub> <sup>6</sup>	193.2	188.0	−5.2	g	5 <sup>h</sup>	50 <sub>0</sub> <sup>2</sup>	198.6	203.2	4.6	−21	−14
40 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup>	282.4	288.3	5.9	−146	−140 ( $\nu_{40}$ )	50 <sub>0</sub> <sup>2</sup> 51 <sub>0</sub> <sup>2</sup>	244.5	249.7	5.2	−9	1 ( $\nu_{51}$ )
39 <sub>0</sub> <sup>1</sup> 42 <sub>0</sub> <sup>1</sup>	349.1	358.0	8.9	n.a.	−110 ( $\nu_{39}$ )	49 <sub>0</sub> <sup>1</sup> 50 <sub>0</sub> <sup>1</sup>	284.0	284.0	0	21	8 ( $\nu_{49}$ )
41 <sub>0</sub> <sup>2</sup>	371.0	375.4	4.4	−14	−36	49 <sub>0</sub> <sup>1</sup> 50 <sub>0</sub> <sup>1</sup> 51 <sub>0</sub> <sup>4</sup>	378.4	378.8	0.4		
						48 <sub>0</sub> <sup>2</sup>	426.2	430.3	4.1	−50	−62

<sup>a</sup> From Ref. [19].

<sup>b</sup> The energy of the vibronic transition above the origin (from Tables 1 and 2).

<sup>c</sup> The difference between columns 3 and 2.

<sup>d</sup> The frequency change of the vibrational normal mode involved in the transition upon excitation of the bare molecule from  $S_0$  to  $S_1$ . Experimental values, Ref. [5] and this work; calculated ones from Ref. [19]. When more than one mode is involved in the transition, the one for which data are given is shown in parentheses; n.a. signifies that experimental data are not available.

<sup>e</sup> From Ref. [37].

<sup>f</sup> The difference between columns 8 and 7.

<sup>g</sup> According to Ref. [3], there is a large increase in the frequency of this vibration. The analysis of Ref. [19] shows a modest one. In both models, the molecule in  $S_1$  is more rigid in the torsional mode than in  $S_0$ .

<sup>h</sup> According to a RHF/3-21G calculation.

tion this effect does not exist, and no effect on the vibrational frequency is expected. Likewise, the interactions between the argon, situated  $\approx 3.5$  Å away from the molecular plane (Table 3), with in-plane motions of the atoms are expected to be much weaker than with out-of-plane motions. Thus, the force constant and frequency of in-plane modes should hardly be affected by the formation of the complex, as observed experimentally.

The only case for which a negative  $\Delta\nu(S_0-S_1)$  was found for an out-of-plane vibronic mode is the  $\Delta E = 193.2$  cm $^{-1}$  of styrene, that shows a  $-5$  cm $^{-1}$  shift. The assignment of this band given by Hollas et al. [1] is  $41_0^2$ , whereas we offered a different option,  $42_0^6$ . According to Hollas, the  $\nu_{41}$  mode frequency is reduced from 199 cm $^{-1}$  in  $S_0$  to 97 cm $^{-1}$  in  $S_1$ . We have calculated a frequency of 28 and 33 cm $^{-1}$  for  $S_0$  and  $S_1$ , respectively, for  $\nu_{42}$  [19,36]<sup>1</sup>. Although the accuracy of the calculation is not such that this change can be considered as significant, it is in line with the notion that the molecule stiffens in the torsional mode ( $\nu_{42}$  in STY). Complexation with argon can be imagined to counteract the stiffening modifying somewhat the  $\pi$ -electron distribution toward the ground state distribution. A similar argument would predict a positive  $\Delta\nu(S_0-S_1)$ , if Hollas' assignment is adopted.

## 5. Summary

The properties of some adducts of STY and BMS were studied in a supersonic jet. The REMPI method was used to measure the dissociation energies of the clusters, and some vibrational frequencies in the first electronically excited state,  $S_1$ . Dissociation energies can be measured with relatively high accuracy, since a large number of vibronic transitions are observed near the dissociation threshold. Furthermore, good coupling between intra- and inter-molecular modes appears to take place, leading to rapid dissociation of the cluster once the threshold is exceeded. The calculated empirical potential surfaces reproduce the experimental dissociation energies and the stretching

vibrations reasonably well. The vertical displacement of the argon atom from the ring at equilibrium is calculated to be close to that measured experimentally for the benzene–argon adduct.

The internal vibrational frequencies of the styrenes in  $S_1$  appear to be measurably affected by the van der Waals bonded argon atom, though to a small extent (a few wavenumber units). Furthermore, out-of-plane modes seem to be more strongly affected than in-plane ones. The effect may be likened to the solvent shift observed upon trapping molecules in a rare gas matrix, and we find that the shifts observed are of the same order of magnitude as the matrix ones, *even though only one argon atom is present*. This seems to imply that in the case of the low frequency vibrations of styrene, the solvent shift is dominated by a single argon atom. In general, we find a blue-shift upon adduct formation. This may be due either to increasing the force constant, or decreasing the reduced mass of the oscillating mode (or both). The argon atom is located above the aromatic ring and its bonding to the molecule is slightly strengthened upon electronic excitation. A qualitative rationale for the observed shifts is that the interaction with the argon atom in the excited state is enhanced, since the  $\pi$ -electron system overlaps better with its electrons. The in-plane modes are affected to a lesser extent than the out-of-plane ones, since the 'swelling' of the  $\pi$ -electron system influences the latter to a greater degree, as evidenced by the bigger changes in their frequencies upon  $S_0 \rightarrow S_1$  excitation [37].

## Acknowledgement

The Farkas Center for Light-Induced Processes is supported by the Minerva Gesellschaft mbH, Munich. This research was supported by the Binational German–Israel James Franck Research Program for Laser Matter Interaction. We thank Dr. S. Zilberg and E. Zingher for many helpful discussions and Professor C. Lifshitz and Y. Laskin for performing the RRKM calculation.

## References

- [1] J.M. Hollas, E. Khalilipour and S.N. Thakur, J. Mol. Spectry. 73 (1978) 240.

<sup>1</sup> A RHF/3-21G calculation of STY using the Gaussian program package.

- [2] J.M. Hollas and T. Ridley, *Chem. Phys. Letters* 75 (1980) 94.
- [3] J.M. Hollas and T. Ridley, *J. Mol. Spectry.* 89 (1981) 232.
- [4] L. Chia, L. Goodman and J.G. Philis, *J. Chem. Phys.* 79 (1983) 593.
- [5] J.A. Syage, F. Al Adel and A.H. Zewail, *Chem. Phys. Letters* 103 (1983) 15.
- [6] P.H. Hepburn and J.M. Hollas, *Mol. Phys.* 26 (1973) 377.
- [7] V.H. Grassian, E.R. Bernstein, H.V. Secour and J.I. Seeman, *J. Phys. Chem.* 93 (1989) 3470.
- [8] V.H. Grassian, E.R. Bernstein, H.V. Secour and J.I. Seeman, *J. Phys. Chem.* 94 (1990) 6691.
- [9] J.M. Hollas and M.H. Bin Hussein, *Chem. Phys. Letters* 103 (1989) 14.
- [10] J.M. Hollas and P.H. Taday, *J. Chem. Soc. Faraday Trans.* 87 (1991) 3335.
- [11] J.M. Hollas and P.H. Taday, *J. Chem. Soc. Faraday Trans.* 87 (1991) 3585.
- [12] J.M. Hollas and M.H. Bin Hussein, *J. Mol. Spectry.* 145 (1991) 89.
- [13] S. Piccirillo, M. Coreno, A. Giardini-Guidoni, G. Pizzella, M. Snels and R. Teghil, *J. Mol. Struct.* 293 (1993) 197.
- [14] W.E. Sinclair, H. Yu, D. Phillips, R.D. Gordon, J.M. Hollas, S. Klee and G. Mellau, *in press*.
- [15] R.J. Hemley, D.G. Leopold, V. Vaida and M. Karplus, *J. Chem. Phys.* 82 (1985) 5379.
- [16] R.J. Hemley, U. Dinur, V. Vaida and M. Karplus, *J. Am. Chem. Soc.* 107 (1985) 836.
- [17] M. Head-Gordon and J.A. Pople, *J. Phys. Chem.* 97 (1993) 1147.
- [18] R. Hargitai, P.G. Szalay, G. Pongor and G. Foragasi, *J. Mol. Struct. THEOCHEM* 306 (1994) 293.
- [19] S. Zilberg and Y. Haas, *submitted, for publication*.
- [20] D.H. Whiffen, *J. Chem. Soc.* (1956) 1350.
- [21] O. Dimopoulou-Rademan, U. Even, A. Amirav and J. Jortner, *J. Phys. Chem.* 92 (1988) 5371.
- [22] J.M. Dyke, H. Ozeki, M. Takahasi, M.C.R. Cockett and M. Kimura, *J. Chem. Phys.* 97 (1992) 8926.
- [23] D. Consalvo, A. van der Avoird, S. Piccirillo, M. Coreno, A. Giardini-Guidoni, A. Mele and M. Snels, *J. Chem. Phys.* 99 (1993) 8398.
- [24] W. Drescher, S. Kendler, E. Zingher and Y. Haas, *Chem. Phys. Letters* 224 (1994) 391.
- [25] D. Bahat, O. Cheshenovsky, U. Even, N. Lavie and Y. Magen, *J. Phys. Chem.* 91 (1987) 2460.
- [26] W.C. Wiley and I.H. McLaren *Rev. Sci. Instr.* 26 (1955) 1150.
- [27] T. Droz, S. Leutwyler, M. Mandziuk and Z. Bačić, *J. Chem. Phys.* 101 (1994) 6412.
- [28] M. Mons and J. Le Calve, *Chem. Phys.* 146 (1990) 195.
- [29] F.A. Mornany, L.M. Carruthers, R.F. McGuire and H.A. Scheraga, *J. Phys. Chem.* 78 (1974) 1595.
- [30] A. Corana, M. Marchesi, C. Martini and S. Ridella, *ACM Trans. Math. Software* 13 (1987) 262.
- [31] T. Brubacher, J. Makarewicz and A. Bauder, *J. Chem. Phys.* 101 (1994) 9736.
- [32] Th. Weber, A. von Bargen, E. Riedle and H.J. Neusser, *J. Chem. Phys.* 101 (1994) 6412.
- [33] T.A. Stephenson and S.A. Rice, *J. Chem. Phys.* 81 (1983) 1083.
- [34] Th. Weber, A.M. Smith, E. Riedle, H.J. Neusser and E.W. Schlag, *Chem. Phys. Letters* 175 (1990) 79.
- [35] H. Krause and H.J. Neusser, *J. Chem. Phys.* 99 (1993) 6278.
- [36] M.J. Frisch, G.W. Trucks, M. Head-Gordon, P.M.W. Gill, M.W. Wong, J.B. Foresman, B.G. Johnson, H.B. Schlegel, M.A. Robb, E.S. Replogle, R. Gomperts, J.L. Andres, K. Raghavachari, J.S. Binkley, C. Gonzalez, R.L. Martin, D.J. Fox, D.J. DeFrees, J. Baker, J.J.P. Stewart, J.A. Pople, *GAUSSIAN 92, Revision F2* (Gaussian, Pittsburgh, PA, 1992).
- [37] Y. Haas, S. Kendler, E. Zingher, H. Zuckermann and S. Zilberg, *submitted for publication*.