

# A REMPI study of indene and its clusters with argon and krypton

S. Kendler, S. Zilberg, Y. Haas

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

Received 20 April 1995; in final form 7 June 1995

---

## Abstract

The  $S_0 \rightarrow S_1$  transition of indene was studied in a supersonic jet by resonance enhance multiphoton ionization and assigned with the help of an ab initio calculation. Experimental results are also reported for argon and krypton clusters of indene, from which the dissociation energies of the 1:1 clusters were estimated in both  $S_0$  and  $S_1$  states. Two-color two-photon ionization spectroscopy was used to determine the ionization potential and dissociation energy of the indene–argon cluster ion. The data are compared with results obtained for styrene, whose electronic structure is similar, but has much lower frequency out-of-plane vibrational modes.

---

## 1. Introduction

In indene, as in styrene, a double bond is conjugated to a benzene ring. The  $\pi$  electron structure of the two molecules is expected to be similar, if  $\pi$  delocalization does not extend over the  $\text{CH}_2$  group. It has been suggested long ago [1] that since the origin of the  $S_0 \rightarrow S_1$  transition of indene is practically identical to that of styrene (they differ only by about  $30 \text{ cm}^{-1}$ ), their electronic structure is similar. On the other hand, indene is a much more rigid molecule than styrene, as indicated by the fact that the frequency of its lowest lying vibration is  $187.7 \text{ cm}^{-1}$  [2]. One might therefore expect some differences in the dynamic behaviour of indene and its clusters as compared to the styrene analogs, for instance in the energy flow between inter- and intramolecular vibrations and the dissociation dynamics.

We have recently reported a study of the spectroscopy of styrene and trans- $\beta$ -methylstyrene (BMS) clusters with argon and  $\text{N}_2$ , and determined their

dissociation energies [3]. An interesting correlation between the shifts of *intramolecular* vibrations in the cluster (in  $S_1$ ) as compared to the bare molecule and the changes incurred on these modes' frequencies by electronic excitation was observed. We hereby report our preliminary results on indene and its clusters; since no previous report on the  $S_0 \rightarrow S_1$  spectrum of indene in a supersonic jet is known to us, we report also the resonance enhanced multiphoton ionization (REMPI) spectrum of the bare molecule, and assign it with the help of previous work [4] and an ab initio calculation.

## 2. Experimental

The experimental REMPI setup has been described previously in detail [3], so only essential parts of the apparatus will be briefly described, highlighting the changes introduced for the present work. A supersonic jet was formed by allowing a

carrier gas (helium or argon) containing indene to expand from a high pressure chamber into high vacuum through a pulsed valve. The jet was skimmed 50–100 nozzle diameters downstream, and the resulting molecular beam was irradiated by a tunable, pulsed dye laser inside the source of a time-of-flight mass spectrometer (TOFMS). Two-photon absorption leads to the ionization of indene and its clusters and the ions thus formed are accelerated into a field-free flight tube, at the far end of which they are detected by a Daly-type detector. The signal is amplified, digitized and recorded by a personal computer. In order to determine the ionization potential, two-color ionization was used. The beams of two counter-propagating, independently pumped dye lasers were allowed to cross the molecular beam at the TOFMS source. One of them was an excimer-pumped and the other Nd:YAG-pumped laser; the delay between the two was controlled by a digital delay generator (SRS model 535) to within  $\pm 20$  ns.

### 2.1. Computational details

Calculations were performed using the GAUSS-92 program package [5], run on a Silicon Graphics Indigo R4000/48MB/2GBHD workstation. The ground state ( $S_0$ ) calculations were performed at the HF/4-31G level of theory, while for  $S_1$  and  $S_2$  we used the configuration interaction singles (CIS) procedure [6] to which Møller–Plesset second-order perturbation theory was applied, also using the 4-31G basis set [7].

In all computations, no constraints were imposed on the geometry of the molecule. Full geometrical optimization was performed for each state, and the attainment of the energy minimum was verified by calculating the vibrational frequencies (no negative or imaginary values). All frequencies quoted below were obtained from the computed ones by multiplying with appropriate scaling factors [8]. The same factors (0.89 for the in-plane and 0.85 for the out-of-plane modes) were used for the  $S_0$  and  $S_1$  states.

### 3. Experimental results

The REMPI spectrum of indene in the 270–290 nm range is shown in Fig. 1. The 0, 0 band is at

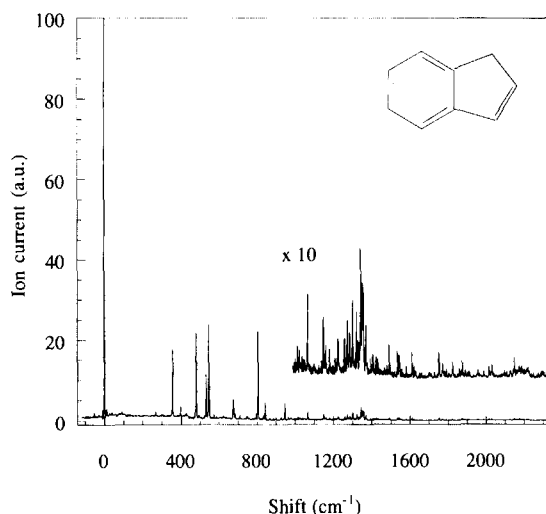


Fig. 1. The REMPI excitation spectrum of indene in a supersonic molecular beam. Indene was held at 0°C and seeded into 7 atm of helium before being expanded. The origin is at 34730  $\text{cm}^{-1}$ . The signal is of the parent ion ( $m/z = 116$  amu).

34730  $\text{cm}^{-1}$ , in agreement with previous bulk measurements [4,9]. The assignments of the main bands, listed in Table 1, are largely based on the ab initio calculation. The nomenclature used is similar to that employed for benzene derivatives belonging to the  $C_s$  symmetry group. The 45 normal modes of indene transform either as the  $a'$  (in-plane modes) or as the  $a''$  irreducible representation (out-of-plane modes). There are 11  $a'$  modes that are numbered consecutively from  $\nu_1$  to  $\nu_{11}$  in decreasing order of their frequency, and 15  $a''$  modes that are numbered  $\nu_{31}$  thru  $\nu_{45}$  in the same order.

Fig. 2 shows the parent ion current observed upon tuning one dye laser to the frequency of the 0, 0 transition, and scanning the other laser between 300 and 328 nm. The steep rise in the signal is assigned to the onset of ionization, leading to an ionization potential of  $65632 \pm 10 \text{ cm}^{-1}$  ( $8.143 \pm 0.001 \text{ eV}$ ). This result is in good agreement with previous determinations ( $8.08 \pm 0.02$  [10], 8.14 [11], 8.15 eV [12,13]), but offers a much better accuracy.

When indene expanded in pure helium was irradiated at or slightly above the origin of the  $S_0 \rightarrow S_1$  transition, 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 indene–argon ( $m/z = 156$ ). The origin

Table 1

Observed bands in the  $S_0 \rightarrow S_1$  REMPI excitation spectrum of indene

Frequency <sup>a</sup> ( $\text{cm}^{-1}$ )		Assignment	Relative intensity
exp.	calc.		
0.0	0.0	origin	100.0
265.9	270	$45_0^2$	0.8
355.9	365	$30_0^1$	16.5
397.0	423	$45_0^1 42_0^1$	2.3
479.4	485	$29_0^1$	21.0
529.9	533	$44_0^1 43_0^1$	11.5
545.2	560	$28_0^1$	24.0
572.4	576	$42_0^2$	1.0
584.7	579	$45_0^1 44_0^3$	0.5
620.0	613	$42_0^1 41_0^1$	0.7
674.3	673	$43_0^1 42_0^1$	4.6
678.4	690	$27_0^1$	3.0
683.4			1.0
709.9	710	$43_0^1 41_0^1$	1.0
746.4			0.7
796.4	798	$44_0^1 37_0^1$	1.2
805.4	811	$26_0^1$	21.5
834.7	835	$42_0^1 39_0^1$	1.0
842.7	847	$25_0^1$	4.1
925.9	927	$41_0^1 38_0^1$	0.5
946.5	955	$23_0^1$	4.0
964.7			0.5
1066.0	1041	$21_0^1$	2.0
1103.5			1.3
1110.6			0.8
1149.4	1149	$39_0^1 38_0^1$	2.0
1161.2	1161	$20_0^1$	0.6
1181.2	1190	$17_0^1$	0.6
1224.5	1222	$42_0^1 35_0^1$	0.7
1258.8	1252	$38_0^1 37_0^1$	0.8
1285.9	1289	$15_0^1$	1.0
1321.8	1319	$43_0^1 35_0^1$	1.5
1342.9			3 <sup>b</sup>
1348.8	1347	$14_0^1$	2.0 <sup>b</sup>
1351.2			2.1 <sup>b</sup>
1355.3			1.6 <sup>b</sup>
1357.6			1.8 <sup>b</sup>
1370.0	1398	$11_0^1$	1.1
1491.8	1500	$10_0^1$	0.7
1534.1	1521	$9_0^1$	0.5
1611.2	1623	$16_0^1$	0.6
1751.8	1750	$28_0^1 17_0^1$	0.6

<sup>a</sup> Frequency shift with respect to the origin at  $34730 \text{ cm}^{-1}$ .

<sup>b</sup> Fermi resonance.

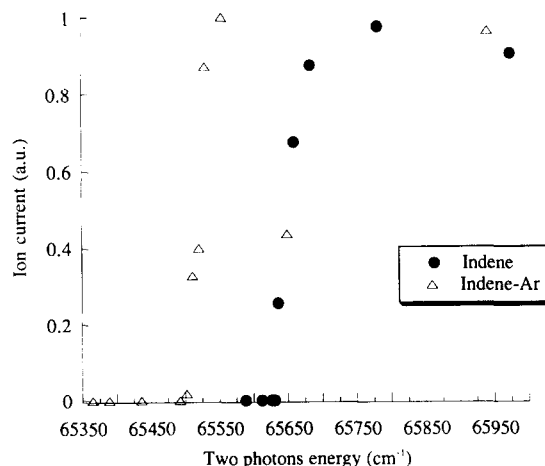


Fig. 2. The two-photon, two-color REMPI signal of indene (parent ion current, filled circles) in the vicinity of the ionization onset. One laser was fixed at the origin of the  $S_0 \rightarrow S_1$  transition, and the other scanned with  $2 \text{ cm}^{-1}$  resolution. The open triangles show the signal for the indene–argon cluster parent ion, obtained in an analogous way. These data were used to determine the ionization potentials.

of the transition due to the 1:1 indene–Ar adduct was red-shifted from the origin of the bare molecule by  $34 \text{ cm}^{-1}$ . The ionization potential of the indene–Ar 1:1 adduct was determined in a way similar to that described above for the bare molecule to be  $65493 \pm 15 \text{ cm}^{-1}$  ( $8.127 \pm 0.002 \text{ eV}$ ), i.e.  $139 \text{ cm}^{-1}$  smaller than that of indene itself.

Expansion of indene with a mixture of krypton and helium led to the observation of the indene–Kr 1:1 adduct ( $m/z = 200$  for the most abundant isotope of krypton). The origin of the transition due to the 1:1 adduct was red-shifted in this case by  $51 \text{ cm}^{-1}$  with respect to the 0, 0 transition of the bare molecule.

Fig. 3 shows the low frequency parts of the excitation spectra of indene and of its 1:1 clusters with argon and krypton. In these spectra the parent ion current intensity was monitored; in the case of the clusters, the bare indene ion peak which was formed upon dissociation of the parent ion could be observed for all the vibronic bands. Fig. 4 shows the ratio of the parent ion to the daughter over the excess energy range of  $0\text{--}650 \text{ cm}^{-1}$ . It is seen that the ratio decreases steeply for argon and krypton clusters beyond  $460 \text{ cm}^{-1}$ . The main excitation peaks of

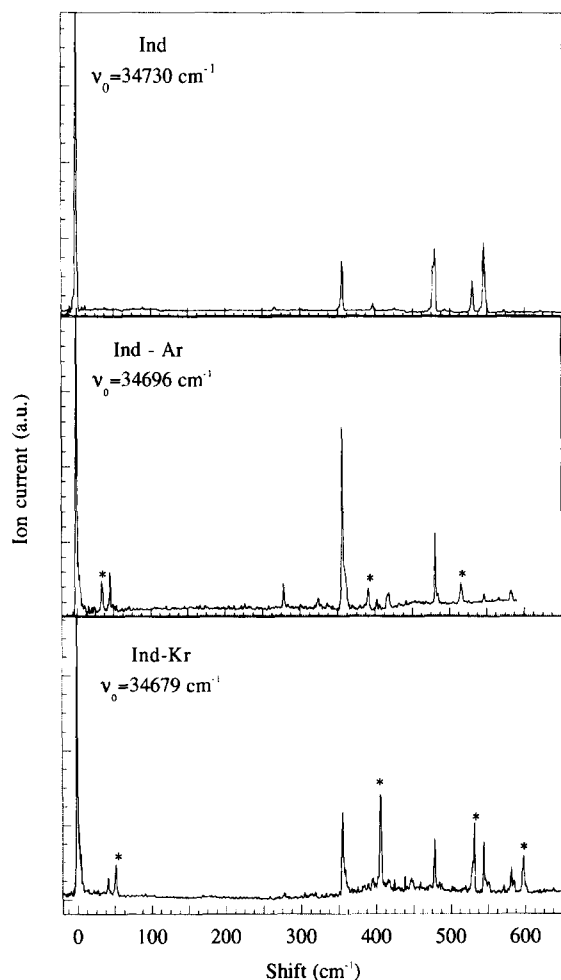


Fig. 3. The low frequency part of the REMPI spectrum of indene, indene–Ar and indene–Kr clusters. The signal shown is that of the parent ion current in each case. Asterisks denote indene molecular peaks that are recorded in the cluster spectrum due to their much higher intensity.

indene and its 1:1 adducts with argon and krypton are listed in Table 2, with their proposed assignments.

#### 4. Calculated results

Most of the ab initio calculations were performed with a 4-31G basis set. Some calculations were performed at the equilibrium geometry with a larger

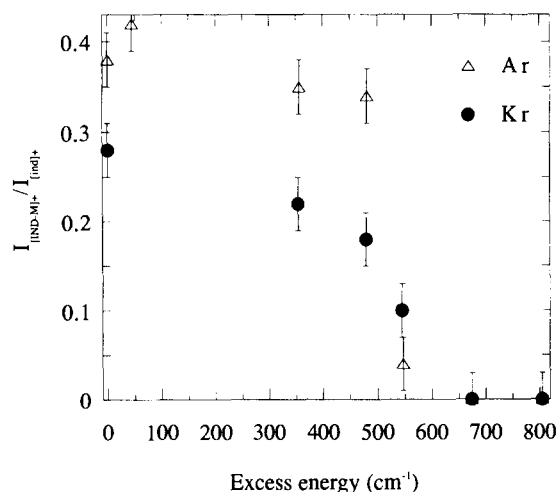


Fig. 4. The ratio of the cluster ion to the daughter molecular ion signal for indene–Ar (open triangles) and indene–Kr 1:1 (filled circles) clusters as a function of excess energy over their respective origins.

basis set to check the validity of the results. The ionization potential was obtained from the orbital energies using Koopman's theorem. These calculations are described in detail in a separate paper [14].

An approximate energy surface was calculated for the clusters by using empirically based potential functions generated from pairwise added atomic Lennard-Jones (LJ) 12–6 potentials [15]. The potential parameters for argon clusters are listed in Table 4 of Ref. [3] (potential I); for krypton clusters, the

Table 2

The observed bands in the MPI excitation spectrum of indene and its 1:1 adducts with argon and krypton (frequencies in  $\text{cm}^{-1}$ )

Assignment	Indene	Indene–Ar	Indene–Kr
origin	34730	34696	34679
vdw1			14.4
vdw2		24.0	27.5
vdw3		45.0	41.3
$45_0^2$	259.9	270.5	270.5
$11_0^1$	355.9	356.4	355.3
$45_0^1 42_0^1$	397.0		
$11_0^1 + \text{vdw3}$		401.7	
$29_0^1$	479.4	480.5	478.6
$44_0^1 43_0^1$	511.0		
$28_0^1$	545.2	545.0	545.6

Table 3  
Experimental and calculated properties of some indene adducts<sup>a</sup>

	Indene–Ar ( $S_0$ )			Indene–Ar ( $S_1$ )	
	exp.	calc.		exp.	calc.
$D_{GS}$ ( $\text{cm}^{-1}$ )	$480 \pm 30$	380	$D_{ES}$ ( $\text{cm}^{-1}$ )	$510 \pm 30$	415
$R_z$ ( $\text{\AA}$ )		3.55	$R_z$ ( $\text{\AA}$ )		3.48
$\nu_{STR}$ ( $\text{cm}^{-1}$ )		39.4	$\nu_{STR}$ ( $\text{cm}^{-1}$ )	44.9	41.2
	Indene–Kr ( $S_0$ )			Indene–Kr ( $S_1$ )	
	exp.	calc.		exp.	calc.
$D_{GS}$ ( $\text{cm}^{-1}$ )	$560 \pm 100$	460	$D_{ES}$ ( $\text{cm}^{-1}$ )	$610 \pm 70$	510
$R_z$ ( $\text{\AA}$ )		3.66	$R_z$ ( $\text{\AA}$ )		3.59
$\nu_{STR}$ ( $\text{cm}^{-1}$ )		34.0	$\nu_{STR}$ ( $\text{cm}^{-1}$ )	41.2	35.4

<sup>a</sup> See Section 5.2 for the experimental determination of the binding energies.  $D_{GS}$  and  $D_{ES}$  are upper limit estimates for the binding energies of the adducts in the  $S_0$  and  $S_1$  states, respectively.

potential parameters were obtained by additivity rules, using published Ar–Ar and Kr–Kr Lennard-Jones potentials<sup>1</sup>.

The global minimum on the potential surface was located by applying the simulated annealing method [17]. Experimental values for the geometry of indene–argon 1:1 adducts are not available; the vertical calculated displacement of the argon atom from the aromatic ring,  $R_z$ , is 3.55  $\text{\AA}$ , close to the measured value for the benzene–argon adduct, 3.50  $\text{\AA}$  [18]. For  $S_1$ , a small decrease in  $R_z$  is calculated, in agreement with observed decrease of 0.045  $\text{\AA}$  observed for the benzene–Ar cluster [19].

The van der Waals stretching frequencies were estimated by assuming that the mode can be approximated as the relative motion of the two constituents 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  $\beta = \omega_e(2\pi^2 c \mu / Dh)^{1/2}$  and  $q = R - R_e$  are used.  $D$  is the dissociation energy,  $R$  the distance between the center of mass of indene and the center of mass of 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 calculated binding energies and stretch frequencies are compared in Table 3 with observed values.

## 5. Discussion

### 5.1. The bare molecule

The MPI excitation spectrum is in good agreement with the room temperature absorption spectrum of Ref. [4], as well as with the ab initio calculation. The assignment offered in Table 1 is tentative, being based mostly on the calculation. The very short progressions indicate a small change in geometry upon excitation, also in agreement with the calculation, and with the experimental data of Ref. [9]. The value of the measured ionization potential (8.143 eV) is close to previous determinations [10–13], but since no hot bands interfere with the spectra, it is probably accurate to better than 0.002 eV. It is also in good agreement with the result of a HF calculation using a 6-31G\* basis set, 8.08 eV.

### 5.2. Indene adducts energetics and dynamics

The binding energies of the indene–Ar and indene–Kr 1:1 adduct in  $S_0$  and  $S_1$  have not been measured before. As in the case of styrene [3], the MPI measurement is based on the change in the parent ion signal intensity as a function of excess energy in  $S_1$ , as shown in Fig. 4. In a one-color, two-photon REMPI experiment, the decrease could

<sup>1</sup> The potential parameters for the krypton clusters were  $\epsilon_{C-Kr} = 41.8$  (48.5)  $\text{cm}^{-1}$ ,  $\epsilon_{H-Kr} = 39.4$  (39.4)  $\text{cm}^{-1}$ ,  $\sigma_{C-Kr} = 3.58$  (3.51)  $\text{\AA}$ ,  $\sigma_{H-Kr} = 3.31$  (3.31)  $\text{\AA}$ . Entries in parentheses are for the  $S_1$  state. These values were obtained from the argon potential parameters using  $\epsilon_{Kr-Kr} = 119$   $\text{cm}^{-1}$ ,  $\epsilon_{Ar-Ar} = 83.5$   $\text{cm}^{-1}$ ,  $\sigma_{Kr-Kr} = 3.6$   $\text{\AA}$ ,  $\sigma_{Ar-Ar} = 3.4$   $\text{\AA}$  [16].

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, in analogy with the styrene–Ar adduct case [3].

The ionization potential of the indene–Ar 1:1 adduct is  $139\text{ cm}^{-1}$  smaller than that of bare indene. The binding energy of the  $[\text{indene-Ar}]^+$  ion cluster is therefore  $139\text{ cm}^{-1}$  larger than that of the neutral. For similar sized molecules such as benzene and styrene, the binding energies are of the order of  $500\text{ cm}^{-1}$  ( $0.06\text{ eV}$ ) [3,20]. The combined energy of two photons at the resonance energy of the 0, 0 transition of the adduct ( $8.61\text{ eV}$ ), is about  $0.5\text{ eV}$  higher than the ionization potential of indene–Ar cluster; the appearance of the molecular ion ( $\text{indene}^+$ ) upon excitation at this frequency is therefore accounted for. Assuming that the indene–Ar<sup>+</sup> ion binding energy is similar to that of the analogous styrene cluster, one expects that, if all the excess energy remains in the ion (i.e. for zero energy electrons), the cluster ion would dissociate. However, since a large fraction of the excess energy may end up in the free electron, many cluster ions are formed with little internal energy and do not dissociate while in the acceleration zone of the TOFMS (typically  $1.5\text{ }\mu\text{s}$  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 intramolecular and van der Waals modes alike), an RRKM calculation of the unimolecular rate constant indicates 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. 4 shows for the indene–Ar cluster, the  $I_{(\text{indene-Ar})^+}/I_{\text{indene}^+}$  ratio is approximately constant at  $0.4 \pm 0.14$  up to  $\Delta E \approx 460\text{ cm}^{-1}$ , and then drops to zero over a  $50\text{ cm}^{-1}$  span. A similar result is observed for the indene–Kr cluster, although the intensity decrease appears to be more gradual. 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. From these data we estimate that the dissociation energy of the indene–Ar and of the indene–Kr clusters are  $510 \pm 30$  and  $610 \pm 70\text{ cm}^{-1}$ , respectively, in the  $S_1$  state. The spectral shifts of the origins of the cluster  $S_0 \rightarrow S_1$  transition ( $34$  and  $51\text{ cm}^{-1}$  for Ar and Kr, respectively), combined with these data, lead to estimated dissociation energies of the excited clusters,  $480 \pm 30$  and  $560 \pm 70\text{ cm}^{-1}$ . In a similar way, the dissociation energy of the indene–Ar 1:1 ion cluster is calculated to be  $620 \pm 30\text{ cm}^{-1}$ , justifying the assumption made at the beginning of this section.

The rapid dissociation of the molecular adduct as its internal energy exceeds the dissociation energy is based on the assumption of rapid intramolecular vibration redistribution (IVR) in the cluster, involving both intramolecular vibrations and van der Waals ones. This appears to be the case for molecules with low frequency internal vibrations, such as styrene and BMS [3,21]. In the case of styrene the lowest frequency vibration has a quantum of  $38$  and  $97\text{ cm}^{-1}$ , respectively, in  $S_0$  and  $S_1$ . These values are not much larger than the frequency of the cluster intermolecular stretching vibration, so that coupling between the two is expected to be efficient. However, this is not necessarily the general case, and indeed benzene–argon clusters [22] are known to fluoresce on excitation to the  $6^1$  vibration of  $S_1$ , which lies at  $\Delta E = 521\text{ cm}^{-1}$ . Furthermore, high resolution spectra of this cluster [19] and of the benzene–N<sub>2</sub> cluster [23] 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. [24] for benzene–Ar,  $408\text{ cm}^{-1}$  according to Ref. [18]). In benzene, there are no low lying intramolecular vibrations (lowest frequency is  $398.8$  and  $237.5\text{ cm}^{-1}$ , respectively, in  $S_0$  and  $S_1$  [25]), and it appears that the coupling to the van der Waals ones is slow enough to permit observation of fluorescence. In indene, the lowest lying ground state mode is at  $187.7\text{ cm}^{-1}$ , and in  $S_1$ , at  $133\text{ cm}^{-1}$  (Table 1). It is possible that in this case coupling to the intermolecular van der Waals vibration is slower than in styrene, and that the apparent dissociation energies found experimentally are higher than the actual ones. The relatively small number of vibronic bands in the

region of interest (as compared to styrene or BMS [3], for instance) also makes it difficult to determine the dissociation energy.

The calculation based on the atom–atom pairwise potentials consistently results in *lower* dissociation energies than experimentally observed (Table 3). The calculated values are similar to the expected ones for similar sized molecules, and we propose that the higher experimental values are due to the fact that mode coupling between molecular and cluster modes is not as efficient as statistical theories assume.

In the excitation spectra of styrene and BMS clusters, some out-of-plane *intramolecular* bands were found to be shifted to the blue with respect to those of the bare molecule. This trend was found for those modes that underwent a strong *red* shift upon excitation of the bare molecule from  $S_0$  to  $S_1$  [3]. It was tentatively assigned to the fact that in the cluster, the density of the  $\pi$  electrons in the excited molecule is slightly increased upon complexation as compared to that of the bare molecule, counter-acting the effect of electronic excitation that tends to reduce this density. Inspection of Table 2 shows that in the case of indene, most of the bands (that belong to in-plane modes) show a small shift upon adduct formation. The out-of-plane  $45_0^2$  band is significantly blue-shifted in the clusters (by about  $11.6\text{ cm}^{-1}$ ), in agreement with the findings on the styrenes. More extensive data will be required for further discussion, and these require higher frequency vibronic bands. Experiments on clusters with higher binding energies are planned for this purpose.

## 6. Summary

The REMPI spectra of indene and some of its clusters are reported for the first time. The spectra are in good agreement with *ab initio* calculations of the frequencies of the  $S_1$  state. The REMPI method has been used to estimate the binding energies of the clusters in the ground and first electronically excited state, as well as of the indene–argon ion cluster. The cluster dissociation energies, estimated from the spectra, are consistently larger than those calculated using an empirical atom–atom pairwise potential. This trend is in agreement with similar results on benzene clusters, and in contrast with results on

styrene clusters. It may be related to the fact that in the more rigid molecules (benzene and indene), coupling between intramolecular vibrations and cluster van der Waals intermolecular vibrations is not as efficient as in the more flexible styrene molecule.

## Acknowledgements

The Farkas Center for light–matter interaction is supported by the Minerva Gesellschaft mbH, Munich.

## References

- [1] A.I. Kiss and B.R. Muth, *Acta Chim. Acad. Hung.* 11 (1957) 365.
- [2] W. Caminati, *J. Chem. Soc. Faraday Trans.* 89 (1993) 4153.
- [3] S. Kendler and Y. Haas, *Chem. Phys. Letters* 236 (1995) 324.
- [4] J.M. Hollas, *Spectrochim. Acta* 16 (1963) 753.
- [5] 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 and J.A. Pople, *GAUSSIAN 92*, Revision F2 (Gaussian, Pittsburgh, 1992).
- [6] J.B. Foresman, M. Head-Gordon, J.A. Pople and M.J. Frisch, *J. Chem. Phys.* 96 (1992) 135.
- [7] W.J. Hehre, R. Ditchfield and J.A. Pople, *J. Chem. Phys.* 56 (1972) 2257.
- [8] J.A. Pople, A.P. Scott, M.W. Wong and L. Radom, *Israel J. Chem.* 33 (1993) 345.
- [9] A. Hartford and J.R. Lombardi, *J. Mol. Spectry.* 34 (1970) 257.
- [10] J. Aihara and H. Inokuchi, *Bull. Chem. Soc. Japan* 43 (1970) 1265.
- [11] M.J.S. Dewar, E. Haselbach and S.D. Worley, *Proc. Roy. Soc. A* 315 (1970) 431.
- [12] H. Güsten, L. Klasinc and B. Ruscic, *Z. Naturforsch.* a 31 (1976) 1051.
- [13] W.J. Simonsik and R.A. Hites, *Anal. Chem.* 58 (1986) 2114.
- [14] S. Zilberg, S. Kendler and Y. Haas, to be published.
- [15] T. Droz, S. Leutwyler, M. Mandziuk and Z. Bacic, *J. Chem. Phys.* 101 (1994) 6412.
- [16] J.O. Hirschfelder, C.E. Curtiss and R.B. Bird, *Molecular theory of gases* (Wiley, New York, 1954).
- [17] A. Corana, M. Marchesi, C. Martini and S. Ridella, *ACM Trans. Math. Software* 13 (1987) 262.
- [18] T. Brubacher, J. Makarewicz and A. Bauder, *J. Chem. Phys.* 101 (1994) 9736.
- [19] Th. Weber, A. von Barga, E. Riedle and H.J. Neusser, *J. Chem. Phys.* 92 (1990) 90.

- [20] J.M. Dyke, H. Ozeki, M. Takahasi, M.C.R. Cockett and M. Kimura, *J. Chem. Phys.* 97 (1992) 8926.
- [21] O. Dimopoulou-Rademan, U. Even, A. Amirav and J. Jortner, *J. Phys. Chem.* 92 (1988) 5371.
- [22] T.A. Stephenson and S.A. Rice, *J. Chem. Phys.* 81 (1983) 1083.
- [23] Th. Weber, A.M. Smith, E. Riedle, H.J. Neusser and E.W. Schlag, *Chem. Phys. Letters* 175 (1990) 79.
- [24] H. Krause and H.J. Neusser, *J. Chem. Phys.* 99 (1993) 6278.
- [25] R.H. Page, Y.R. Shen and Y.T. Lee, *J. Chem. Phys.* 88 (1988) 5362.