

Electronic Supplementary Information to:  
**Formation of resonances and anionic fragments upon electron  
attachment to benzaldehyde**

J. Ameixa,<sup>ab</sup> E. Arthur-Baidoo,<sup>a</sup> J. Pereira-da-Silva<sup>b</sup>, M. Ryszka<sup>c</sup>, I. Carmichael<sup>c</sup>, L.M. Cornetta<sup>d</sup>, M.  
T. do N. Varella<sup>d</sup>, F. Ferreira da Silva<sup>b</sup>, S. Ptasińska<sup>ce</sup> and S. Denifl<sup>a</sup>

<sup>a</sup>Institut für Ionenphysik und Angewandte Physik and Center for Molecular Biosciences (CMBI), Leopold-Franzens  
Universität Innsbruck, Technikerstraße 25/3, 6020 Innsbruck, Austria. E-mail: Stephan.denifl@uibk.ac.at

<sup>b</sup>Atomic and Molecular Collisions Laboratory, CEFITEC, Department of Physics, Universidade NOVA de Lisboa, 2829-  
516 Caparica, Portugal E-mail:

<sup>c</sup>Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556, USA

<sup>d</sup>Instituto de Física, Universidade de São Paulo, Rua do Matão 1731, 05508-090 São Paulo, Brazil

<sup>e</sup>Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556, USA

**1. Formation of anions through dissociative electron attachment to benzaldehyde**

Table SI. G4(MP2) thermodynamic thresholds for anionic fragments formed through a single  
bond cleavage, in eV, at T= 0 K (third column) and T = 298.15 K (fourth column).

hydrogen elimination	$\text{BA} + e^- \rightarrow (\text{BA} - \text{H})^- + \text{H}(9)$	3.21	2.92
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{H})^- + \text{H}(10)$	3.11	2.83
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{H})^- + \text{H}(11)$	3.15	2.86
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{H})^- + \text{H}(12)$	2.97	2.68
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{H})^- + \text{H}(13)$	3.09	2.80
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{H})^- + \text{H}(14)$	3.28	2.98
oxygen elimination	$\text{BA} + e^- \rightarrow (\text{BA} - \text{O})^{\bullet-} + \text{O}(^3\text{P})$	6.31	5.92
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{O})^{\bullet-} + \text{O}(^1\text{D})$	8.33	7.97
	$\text{BA} + e^- \rightarrow (\text{BA} - \text{O}) + \text{O}^-$	6.38	6.02
formaldehyde-H elimination	$\text{BA} + e^- \rightarrow \text{C}_6\text{H}_5^- + \text{CHO}^\bullet$	3.01	2.53
	$\text{BA} + e^- \rightarrow \text{C}_6\text{H}_5^\bullet + \text{CHO}^-$	3.90	3.38

Table SII. G4(MP2) thermodynamic thresholds for anionic fragments formed through two or three bond cleavages, in eV, at T = 0 K (third column) and T = 298.15 K (fourth column).

OH <sup>•</sup> elimination	BA + e <sup>-</sup> → (BA - OH) <sup>-</sup> + OH(9) <sup>•</sup>	6.36	5.95
	BA + e <sup>-</sup> → (BA - OH) <sup>-</sup> + OH(10) <sup>•</sup>	6.14	5.72
	BA + e <sup>-</sup> → (BA - OH) <sup>-</sup> + OH(11) <sup>•</sup>	6.30	5.89
	BA + e <sup>-</sup> → (BA - OH) <sup>-</sup> + OH(12) <sup>•</sup>	6.32	5.89
	BA + e <sup>-</sup> → (BA - OH) <sup>-</sup> + OH(13) <sup>•</sup>	5.83	5.41
	BA + e <sup>-</sup> → (BA - OH) <sup>-</sup> + OH(14) <sup>•</sup>	6.56	6.15
OH <sup>-</sup> elimination	BA + e <sup>-</sup> → (BA - OH) <sup>•</sup> + OH(9) <sup>-</sup>	6.35	5.93
	BA + e <sup>-</sup> → (BA - OH) <sup>•</sup> + OH(10) <sup>-</sup>	6.30	5.88
	BA + e <sup>-</sup> → (BA - OH) <sup>•</sup> + OH(11) <sup>-</sup>	6.34	5.92
	BA + e <sup>-</sup> → (BA - OH) <sup>•</sup> + OH(12) <sup>-</sup>	6.32	5.90
	BA + e <sup>-</sup> → (BA - OH) <sup>•</sup> + OH(13) <sup>-</sup>	5.15	4.72
	BA + e <sup>-</sup> → (BA - OH) <sup>•</sup> + OH(14) <sup>-</sup>	6.40	5.98
H <sub>2</sub> O elimination	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(13)OH(10)	5.14	4.65
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(13)OH(9)/H(13)OH(11)	5.05	4.58
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(13)OH(12)/H(13)OH(14)	3.38	2.92
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(14)OH(9)	5.97	5.49
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(14)OH(10)	5.54	5.06
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(14)OH(11)	5.95	5.47
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(14)OH(12)	5.74	5.26
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(12)OH(9)	5.84	5.36
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(12)OH(10)	5.44	4.96
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(12)OH(11)	5.21	4.74
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(9)OH(10)	5.13	4.66
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(9)OH(11)	5.61	5.09
	BA + e <sup>-</sup> → C <sub>7</sub> H <sub>4</sub> <sup>•-</sup> + H(10)OH(11)	5.12	4.65

## 2. Shape resonances at low energies (0 ~ 5 eV)

Table SIII. Estimative of positions and (widths) of the shape resonances of benzaldehyde (in eV) obtained by the SMCPP scattering method and the scaled VOs accordingly to Strnad *et. al.*<sup>1</sup>.

	$\pi_1^*$	$\pi_2^*$	$\pi_3^*$	$\pi_4^*$
<b>SMCPP</b>	-0.48	0.78 (0.005)	2.48 (0.09)	5.74 (0.40)
<b>Scaled VOs</b>	-0.05	0.77	2.14	4.54

## 3. Excited states for neutral benzaldehyde (0 ~ 9.5eV)

<sup>1</sup> S. W. Staley and J. T. Strnad, Calculation of the energies of  $\pi^*$  negative ion resonance states by the use of Koopmans' Theorem, *J. Phys. Chem.*, 1994, **98**, 116–121.

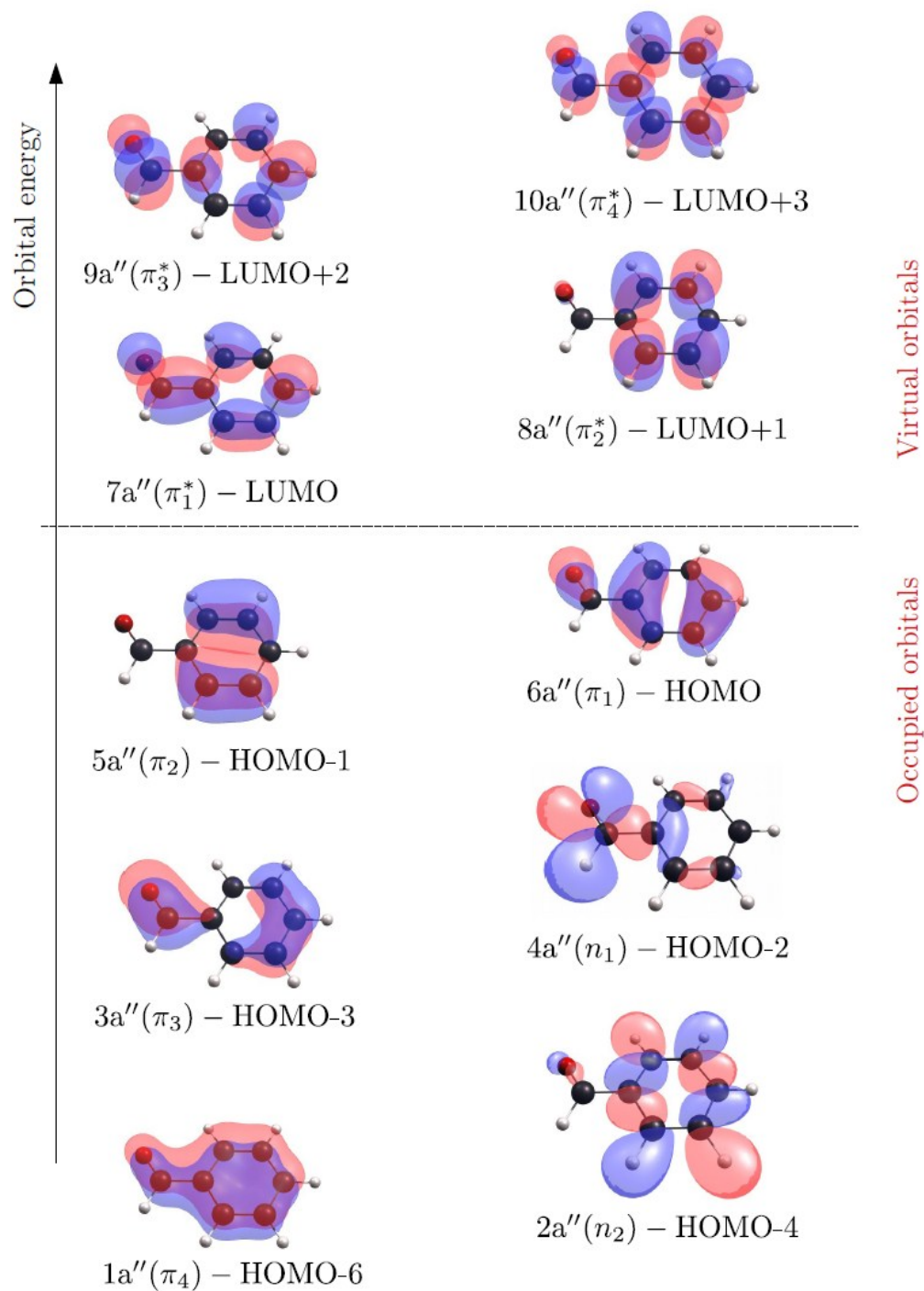


Figure S1. Schematic diagram showing the full active space used in the CASSCF/CASPT2 calculations for neutral species of benzaldehyde.

### 3. Resonance position for $m/z$ 78

The resonance positions were determined by fitting the ion signal with Gaussian functions. The software OriginPro 9 was used to produce the plots, and a function “Gauss” was used to fit the data, as follows:

$$y = y_0 + \frac{A}{w \sqrt{\frac{\pi}{2}}} e^{-2 \frac{(x - x_c)^2}{w^2}}$$

Where  $y_0$  denotes the offset,  $A$  is the amplitude,  $w$  is the width and  $x_c$  represents the centre of the Gaussian function. The figure S3 shows the ion yield for the formation of  $m/z$  78  $C_6H_4D^-$ , from d-benzaldehyde. Please note that the intensity is provided in arbitrary units.

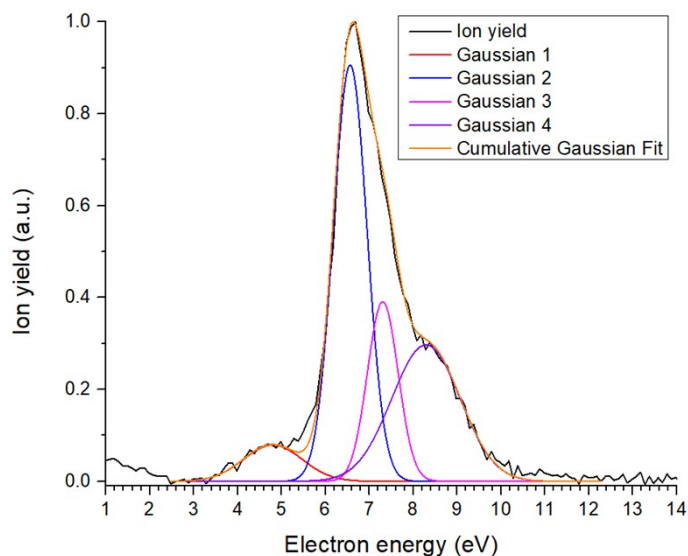


Figure S2. Formation of the deuterated phenyl anion,  $m/z$  78  $C_6H_4D^-$ , from d-benzaldehyde measured with the Notre Dame instrument. The ion signal was fitted with four gaussians, and the orange line represents the cumulative sum of the gaussians.

Table SIV. Fitting parameters corresponding to the gaussian functions used to fit the ion signal of  $m/z$  78  $C_6H_4D^-$ , from d-benzaldehyde measured with the Notre Dame instrument

		<b>Gaussian 1</b>	<b>Gaussian 2</b>	<b>Gaussian 3</b>	<b>Gaussian 4</b>
<b>y<sub>0</sub></b>	<b>Value</b>	0	0	0	0
<b>y<sub>0</sub></b>	<b>Standard Error</b>	0	0	0	0
<b>x<sub>c</sub></b>	<b>Value</b>	4.78	6.61224	7.487	8.49876
<b>x<sub>c</sub></b>	<b>Standard Error</b>	0	0	0	0
<b>w</b>	<b>Value</b>	1.39865	0.85197	0.76718	1.41417
<b>w</b>	<b>Standard Error</b>	0	0.01046	0.03066	0.0521
<b>A</b>	<b>Value</b>	4.5	32.96043	10.86493	14.78188
<b>A</b>	<b>Standard Error</b>	0	0.37068	0.42456	0.50027
<b>sigma</b>	<b>Value</b>	0.69932	0.42598	0.38359	0.70709
<b>FWHM</b>	<b>Value</b>	1.64678	1.00312	0.90329	1.66506
<b>Height</b>	<b>Value</b>	2.5671	30.86804	11.2997	8.34002
Statistics Reduced Chi-Sqr 0.33605					
Statistics Adj. R-Square 0.99565					