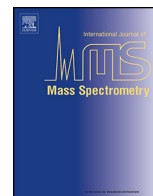




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The photoelectron spectrum of the benzaldehyde anion

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ABSTRACT

The benzaldehyde radical anion was produced in the gas phase and studied using negative ion photoelectron spectroscopy. Analysis of the photoelectron spectrum found the adiabatic electron affinity, $EA_a(\text{C}_6\text{H}_5\text{CHO})$, to be 0.35 ± 0.05 eV. Two active modes of benzaldehyde are observed in the photodetachment of the $\text{C}_6\text{H}_5\text{CHO}^-$ anion: ν_7 , the C=O stretch (1728 cm^{-1}) and ν_6 , the non-phenyl C–H stretch (2806 cm^{-1}). DFT electronic structure calculations have been carried out and are in agreement with the experimental spectrum. The optimized geometries of both $\text{C}_6\text{H}_5\text{CHO } \tilde{X}^1A'$ and $\text{C}_6\text{H}_5\text{CHO}^- \tilde{X}^2A''$ are planar. The excess electron in the benzaldehyde anion is found to be delocalized in its π^* (a'') anti-bonding orbital.

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1. Introduction

Mass spectrometry has made possible the development of many experimental techniques in physical chemistry. Among them is anion photoelectron spectroscopy, carried out with mass-selected negative ions. A variety of types of mass spectrometers have been utilized in identifying and mass-selecting atomic, molecular, and cluster anions studied by photoelectron spectroscopy, these including magnetic sector, quadrupole, Wien Filter, and time-of-flight instruments. Here, we present a study of the benzaldehyde anion, facilitated by a magnetic sector mass analyzer and selector.

Radical anions of aldehydes and ketones are thought to be intermediates and reactants within many important condensed phase reactions of organic chemistry. Alkali metals are used to reduce aldehydes and ketones to produce ketyls, i.e., carbonyl radical anions [1,2]. For example, pinacols [3] are the result of dimerization reactions involving acetone ketyls. Direct studies of the intermediate radical anions produced in the condensed phase are hampered due to solvent interferences. Thus, gas-phase studies provide insight by isolating the radical anion of interest from such interactions.

Benzaldehyde is the simplest aromatic aldehyde (see Fig. 1), and as such it is an important precursor for synthesis of many

organic compounds. Gas-phase infrared and Raman spectroscopic studies supported by calculations [4,5] have provided vibrational assignments of the benzaldehyde molecule. Additional studies have queried its excitation and relaxation dynamics [6–8], photochemical pathways [9–12], and surface chemistry [13]. Nevertheless, even though the neutral benzaldehyde molecule has been well characterized, there are fewer studies dealing with its negative ion, i.e. its radical anion. The electron affinity (EA) of benzaldehyde has been estimated through both experimental [14–16] and theoretical [17] approaches to be ~ 0.4 eV. Furthermore, threshold excitation using the SF_6 scavenger technique [18] and electron transmission spectroscopy (ETS) [19,20] concluded that benzaldehyde must have a small positive electron affinity, and thus should be capable of forming a stable anion. More importantly, there are few negative ion photoelectron studies of intact ketone radical anions [21,22], and those who have attempted to see the radical anions of aldehydes have observed only their deprotonated forms [23], i.e. not the intact aldehyde radical anion.

Here, we present the negative ion photoelectron spectrum of the intact (parent) benzaldehyde radical anion. From its photoelectron spectrum, the adiabatic electron affinity (EA_a) was determined to be 0.35 ± 0.05 eV. This assignment was supported by a Franck–Condon (FC) fit. Our density functional theory (DFT) calculations show that the excess electron occupies the π^* anti-bonding orbital, and that both the anion and its corresponding neutral geometries are planar. The active vibrational frequencies observed in our spectrum compare favorably with the experimentally known vibrational modes of benzaldehyde.

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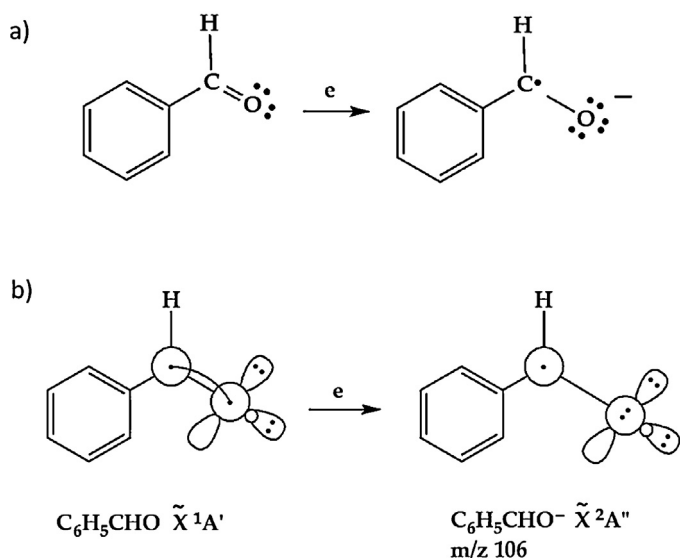


Fig. 1. (a) Pictorial representation of the formation of the benzaldehyde radical anion and uncoupling of the carbonyl group upon attachment of an excess electron. (b) GVB diagram to model the symmetry of the benzaldehyde neutral and corresponding radical anion formed.

2. Methods

2.1. Experimental

Negative ion photoelectron spectroscopy is conducted by crossing a mass-selected beam of anions with a fixed-frequency photon beam and energy-analyzing the resultant photodetached electrons. The photodetachment process is governed by the relationship $h\nu = EBE + EKE$, where $h\nu$ is the photon energy, EBE is the electron binding energy, and EKE is the electron kinetic energy.

The anion photoelectron spectrometer used to measure the photoelectron spectrum of the benzaldehyde parent anion has been described previously [24]. Briefly, the apparatus utilized a supersonic expansion nozzle-ion source (biased at -500 V). Benzaldehyde liquid was placed in the stagnation chamber of this source, heated up to 100°C , and co-expanded with 1–2 atm of argon gas through a $25\ \mu\text{m}$ orifice into a high vacuum region. Negative ions were formed by injecting low energy electrons from a hot and negatively biased, thoriated tungsten filament into the expanding jet, where a microplasma was formed in the presence of a weak external magnetic field. The anions were extracted and transported via a series of ion optics through the flight tube of a 90° magnetic sector mass spectrometer (mass resolution, ~ 400). Mass-selected anions were then crossed with an intracavity argon ion laser beam, where photodetachment occurred. The resultant photodetached electrons were then energy-analyzed by a hemispherical electron energy analyzer with a resolution of $30\ \text{meV}$. The photoelectron spectrum reported here was recorded with $488\ \text{nm}$ ($2.540\ \text{eV}$) photons and calibrated against the well known photoelectron spectrum of the O^- anion [25].

2.2. Computational

DFT calculations were conducted by applying Becke's three-parameter hybrid functional (B3LYP) [26–28] and using the GAMESS [29] software package to determine the electron affinity (EA) of benzaldehyde. Geometries of the anion and its corresponding neutral were fully optimized without geometrical constraints with the aug-cc-pVDZ basis set [30,31]. The electronic energies were improved by single-point calculations with a larger basis

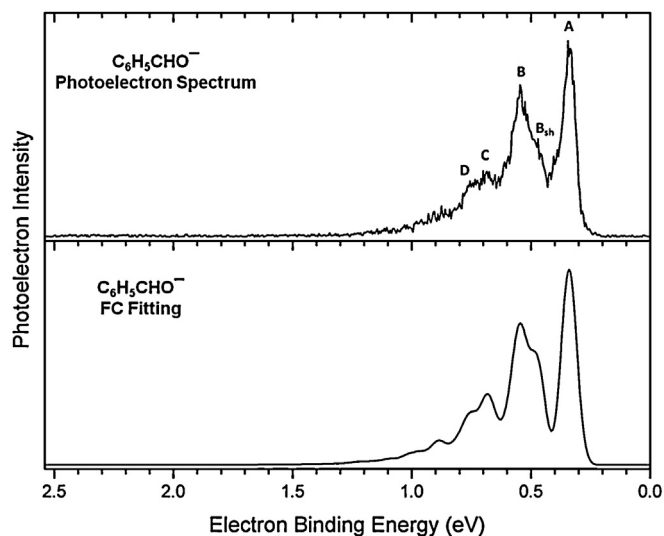


Fig. 2. (Upper trace) The measured photoelectron spectrum of the benzaldehyde anion recorded using $2.540\ \text{eV}$ photons and (lower trace) its corresponding Franck–Condon profile fitting.

set, i.e., aug-cc-pVTZ, at the optimized geometries [30,31]. With the aug-cc-pVDZ basis set, Hessian calculations were also performed to calculate the vibrational frequencies of the neutral and its anion. Franck–Condon factors for fitting the photoelectron spectrum of the benzaldehyde anion were calculated with the Hutchisson Method (independent harmonic oscillators) using the PESCAL program [32].

3. Results and discussion

The photoelectron spectrum of the benzaldehyde parent anion is shown in Fig. 2; it exhibits a vibrationally resolved profile. Its peaks are centered at electron binding energies (EBE) of $0.35\ \text{eV}$ (peak A), $0.56\ \text{eV}$ (peak B), $0.69\ \text{eV}$ (peak C) and $\sim 0.76\ \text{eV}$ (peak D). There is also a shoulder on the low EBE side of peak B, i.e., at $0.48\ \text{eV}$ (peak B_{sh}). [See Table 1.] We assign peak A as the $v'' = 0 \rightarrow v' = 0$ transition, i.e., the origin transition, and thus the adiabatic electron affinity value, is determined to be $EA_a(C_6H_5CHO) = 0.35 \pm 0.05\ \text{eV}$. This EA_a value is in good agreement with our DFT calculation of $0.37\ \text{eV}$ and with previous literature estimates [14–17]. If we include the zero-point energy correction calculated with the vibrational frequency analysis, this increases the EA_a value by approximately $\sim 0.1\ \text{eV}$. We see no significant indication of vibrational hot bands in the spectrum. This may be better explained using a generalized valence bond (GVB) diagram, [33] showing electron attachment to the $C_6H_5CHO \tilde{X}^1A'$ to produce the radical anion, \tilde{X}^2A'' (see Fig. 1b). Since the electron is added to a closed shell molecule, the electron affinity is expected to be small, i.e. less than $0.5\ \text{eV}$. This implies that hot bands may not be visible, since most electrons in the anion can autodetach.

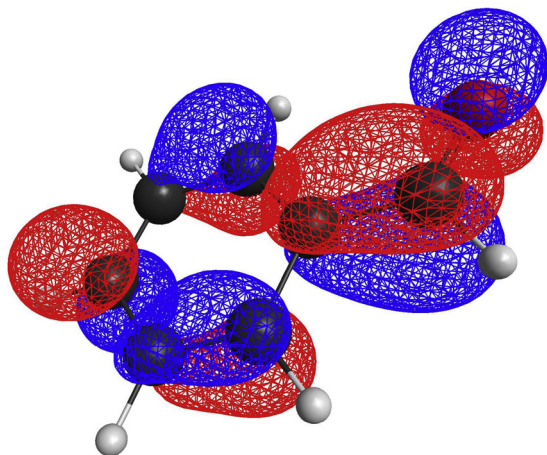
The optimized geometries of both the benzaldehyde anion and its neutral counterpart were calculated and found to be planar, although there are differences in their bond lengths. The highest occupied molecular orbital (HOMO) structure for the benzaldehyde anion is shown in Fig. 3. The excess electron is delocalized in the π^* anti-bonding orbital. The calculated Mulliken charge distribution shows the C=O bond of the aldehyde chromophore to be strongly polarized, i.e. negatively charged, where the carbon atom is -0.46 and oxygen atom is -0.90 .

The photoelectron spectrum in Fig. 2 demonstrates that there is a significant geometry change between the anion and the neutral: $C_6H_5CHO\cdot^- \tilde{X}^2A'' + h\nu_{488\text{nm}} \rightarrow e^- + C_6H_5CHO \tilde{X}^1A'$. The structures

Table 1

Vibrational frequencies extracted from the experimental photoelectron spectrum and compared with calculations from this study and those report in the literature.

Peak location (eV)	Expt. ^a vibrational spacing			B3LYP/aug-cc-pVTZ ^b (cm ⁻¹)	Expt. IR spectra ^c (cm ⁻¹)	Assignment
	Δ	(eV)	(cm ⁻¹)			
A	0.35			0.37		Electron affinity (0,0)
B_{sh}	0.48	B_{sh}-A	0.13	1049	1212	$\nu_{18} = 1074$
B	0.56	B-A	0.21	1694	1725	$\nu_7 = 1728$
C	0.69	C-A	0.34	2742	2816	$\nu_6 = 2806$
D	0.76	D-B	0.20	1613	1725	

^a Deduced from the vibrational spacing between peaks within the recorded photoelectron spectrum.^b Calculations from present work using GAMESS software package.^c Ref. [4].**Fig. 3.** The highest occupied molecular orbital (HOMO) of the ground state of the benzaldehyde anion, as determined at the B3LYP/aug-cc-pVDZ level of theory.

in Fig. 1 predict that the $C_6H_5C(H)=O$ and C_6H_5CO-H stretches will be the active modes upon photodetachment. Benzaldehyde is a planar molecule [34] as is that of the $C_6H_5CHO^-$ anion. The infrared spectrum of C_6H_5CHO has been measured and assigned in the gas phase [4] and in CCl_4 solution [5]. Since they are planar species, the 36 vibrational modes of both benzaldehyde and its radical anion can be classified as even or odd: $36 \text{ fundamentals} = 25a' \oplus 11a''$. Only the a' modes will be active in a photoelectron experiment. The vibrational frequencies from Fig. 2 were measured as the energy spacings between peak centers in the spectrum and are presented in Table 1. Features B and C in the spectrum are easily assigned to ν_7 , the carbonyl stretch, and ν_6 , the non-phenyl C–H stretch. The small peak at D is likely the overtone of ν_7 while the soft shoulder, **B_{sh}**, is more difficult to assign.

We also conducted a Franck–Condon analysis and fit. For comparison, the resulting simulated photoelectron spectrum is shown directly below the experimental spectrum in Fig. 2. The calculated spectral profile matches reasonably well with the measured photoelectron spectrum and is consistent with the origin transition, $\nu(0,0)$, being at 0.35 ± 0.05 eV. As compared to neutral benzaldehyde, the benzaldehyde anion showed significant lengthening of the C=O bond (by approximately 0.065 \AA), of the C–C bonds of the benzene ring (by about 0.076 \AA), and to a lesser effect the C–H bond of the aldehyde chromophore (by roughly 0.002 \AA). These are the dominant vibrational frequencies observed in the photoelectron spectrum; the remaining vibrational modes had a negligible effect. This conclusion was reached by ranging both the displacement and frequency parameters for each vibrational mode, while monitoring the resultant Franck–Condon spectral fit to the experimental spectrum. Thus, the fit was obtained by using a select number of

modes for simulation, i.e. the three active stretching modes. All input parameters, related to $\nu(0,0)$ position, resolution, displacement, and frequency, were treated as live variables and optimized to obtain the best fit. The temperature parameter did not affect the Franck–Condon fitting in assigning the EA_a value, consistent with a dearth of hot band activity in the spectrum.

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