



## Research paper

## Anion photoelectron imaging spectroscopy of glyoxal



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## ABSTRACT

We report a photoelectron imaging study of the radical-anion of glyoxal. The 532 nm photoelectron spectrum provides the first direct spectroscopic determination of the adiabatic electron affinity of glyoxal,  $EA = 1.10 \pm 0.02$  eV. This assignment is supported by a Franck-Condon simulation of the experimental spectrum that successfully reproduces the observed spectral features. The vertical detachment energy of the radical-anion is determined as  $VDE = 1.30 \pm 0.04$  eV. The reported EA and VDE values are attributed to the most stable ( $C_{2h}$  symmetry) isomers of the neutral and the anion.

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## 1. Introduction

Small dicarbonyls play important roles in atmospheric chemistry. The simplest of these molecules is glyoxal (OHCCHO), shown in Fig. 1 (top left). Although it is a minor component of the atmosphere, its contributions to the chemistry of volatile organic compounds [1–4] make it important to the modeling of atmospheric processes. Specifically, glyoxal and its derivatives can be oxidized, hydrolyzed, and oligomerized through heterogeneous reactions to form dimers and larger complexes [5–7]. The oligomers in particular are known to be a source of oxidizing radicals and secondary organic aerosols (SOA) [8–10]. Although the effect of glyoxal oligomers on the modeling of SOAs has not been quantified, laboratory experiments suggest their importance [11]. Perhaps most significantly, glyoxal and other dicarbonyls can form light-absorbing imidazoles, photosensitizing the growth of organic aerosols [12–15]. In addition, very recently glyoxal has emerged as a precursor for several small reactive intermediates with interesting properties, such as the OCCO diradical [16] and the OHCCO and HOCCO radicals [17]. It is in fact these species that motivated our initial interest in the anionic chemistry of glyoxal in general, and the glyoxal radical-anion in particular.

Despite its importance, some of the most fundamental properties of the glyoxal molecule and its anion remain unknown or poorly defined. In particular, the electron affinity (EA) of glyoxal has not been measured. The value appearing in contemporary databases,  $EA = 0.62 \pm 0.26$  eV [18], is an indirect estimate determined from the enthalpies of formation of the anion and the neutral in a study of vinylene carbonate [11]. This indirect result is

inconsistent with the Gaussian-3 (G3MP2B3) method predicting ca. 1.0 eV [18].

The photochemistry of neutral glyoxal has received more attention. It was studied using fluorescence and UV-visible spectroscopy, while computational studies have focused on dimerization [19], dissociation [20] and hydrolysis [21]. Laser-induced fluorescence (LIF) measurements located the lowest-excited singlet state 2.728 eV above the ground state [22]. The lowest triplet state was also observed just below the singlet transition, at 2.381 eV [23] and the singlet-triplet coupling has been studied using level-anti-crossing spectroscopy [24–26]. Of particular interest to atmospheric chemistry is glyoxal unimolecular dissociation [20,27]. In one of the known channels, photoexcited OHCCHO forms two CHO radicals [28], while most famous is the ‘triple whammy’ dissociation into two CO molecules and  $H_2$  [29].

Theoretical evidence from the previous as well as present work clearly shows that the  $C_{2h}$  symmetry isomer (Fig. 1) corresponds to the global minima of both the neutral and anion species [30,31]. Therefore, from this point on, whenever we refer to ‘glyoxal’ without specifying the isomer, the  $C_{2h}$  species is implied. The height of the internal rotation barrier between the  $C_{2h}$  and  $C_{2v}$  neutral isomers was investigated experimentally, with the results varying from  $1770 \pm 60$   $cm^{-1}$  by from During, Bucy and Cole in 1975 [32] to  $2077$   $cm^{-1}$  by Butz in 1990 [27] (all values are with respect to the  $C_{2h}$  minimum). Theoretical predictions of the barrier height vary from  $1960$   $cm^{-1}$ , as determined by Scuseria and Schaefer in 1989 [30], to  $2400$   $cm^{-1}$  by Kakumoto in 1987 [31].

We report the first direct experimental determination of the electron affinity of glyoxal and the vertical detachment energy (VDE) of its radical-anion using anion photoelectron imaging spectroscopy. The experimental results, supported by additional theoretical calculations and Franck-Condon simulations, provide new

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insight into the electronic structure of the glyoxal molecule and its anion.

## 2. Experimental and theoretical methods

The experiments were performed using a custom-built anion photoelectron imaging spectrometer described previously [33,34]. The glyoxal solution (Glyoxal, pure, 40% wt/wt solution in water, ACROS Organics) was first partially dehydrated using a ~1:1 volume ratio of 3 Å molecular sieves for at least 24 h until the solution was yellowish rather than colorless and transparent. The solution was then extracted from the sieve mixture using methanol [35]. The resulting solution was heated to 70–85 °C in order to raise its vapor pressure. The vapor was seeded into an N<sub>2</sub>O carrier gas with a backing pressure of 20 psi. The mixture was expanded into the source chamber through a pulsed supersonic nozzle (General Valve, Inc., Series 9) operated at a repetition rate of 50 Hz. The expansion was crossed with a collimated beam of 1 keV electrons from an electron gun. Anions were formed by attachment of slow secondary electrons in the electron-impact ionized plasma [35].

Glyoxal anions were interrogated by linearly polarized laser pulses at 532 nm obtained by frequency doubling the fundamental output of a Spectra Physics LAB-130-50 Nd:YAG laser. The laser pulses were timed to interact only with the ions of a mass-to-charge ratio  $m/z = 58$ . Photoelectrons were velocity-mapped [36] in the direction perpendicular to the ion and laser beams and projected onto a 40 mm diameter dual microchannel-plate detector, coupled to a P43 phosphor screen. Photoelectron impact positions were recorded by a thermoelectrically cooled charge-coupled-device camera. Images were typically accumulated for ~10<sup>6</sup> experimental cycles. The complete three-dimensional photoelectron distribution was reconstructed via an inverse Abel transformation [37] implemented in the BASEX program [38]. The resulting radial distributions were converted to photoelectron spectra using the well-known O<sup>-</sup> photodetachment transitions for calibration [39,40].

Electronic structure calculations and geometry optimizations were performed using the GAUSSIAN 09 software package [41]. Geometry optimizations using the coupled-cluster method with single and double excitations (CCSD) with Dunning's augmented correlation-consistent basis of triple- $\zeta$  quality (aug-cc-pVTZ) were performed for both the anion and neutral species of glyoxal, yielding both the C<sub>2h</sub> and C<sub>2v</sub> symmetry equilibrium structures. These were used in the calculations of adiabatic electron affinities and vertical detachment energies. The EAs were calculated as the difference in the electronic energy for the glyoxal anion and neutral species at the respective optimized geometries (C<sub>2h</sub> or C<sub>2v</sub>). The VDEs were calculated as the energy difference for the anion and the neutral species, both at the optimized geometry of the anion. Zero-point vibrational energy corrections were determined using single-point harmonic frequency calculations at the same level of theory but with the smaller aug-cc-pVDZ basis set, after re-optimizing the structures with the smaller basis.

The CCSD/aug-cc-pVTZ optimized geometries and CCSD/aug-cc-pVDZ vibrational frequencies were also used for the normal mode analysis as part of the Franck-Condon (FC) simulations. These simulations were carried out using the PESCAL 2010 software, with the normal modes treated as uncoupled harmonic oscillators with full Duschinsky rotation using the Chen method [42,43].

## 3. Results and analysis

The raw photoelectron image of glyoxal anion collected at 532 nm is shown in Fig. 2 along with the corresponding spectrum.

The spectrum is plotted versus electron binding energy:  $eBE = hv - eKE$ , where  $hv$  is the photon energy and  $eKE$  is the kinetic energy of the photoelectrons. The image indicates slightly negative photoelectron anisotropy with respect to the laser polarization direction, along with some limited vibrational resolution discernable in the spectrum.

The spectrum consists of the main intense band labeled A with partial vibrational resolution and a weak shoulder (B) extending from under the major feature A towards lower eBEs. Later in this Section, band A will be assigned to the  $X^1A_g \leftarrow X^2A_u$  photodetachment transition in the radical-anion of glyoxal (C<sub>2h</sub> isomer). The anion VDE is defined approximately by the position of the overall band A maximum. It was determined as  $VDE = 1.30 \pm 0.04$  eV by fitting a broad Gaussian envelope to the entire band.

The maximum of the first peak (marked '0' in Fig. 2) corresponds to the adiabatic EA of glyoxal, determined as  $EA = 1.10 \pm 0.02$  eV. This directly determined value is significantly different from the previous indirectly obtained result  $EA = 0.62 \pm 26$  eV [11], presently cited in databases [18]. On the other hand, the new spectroscopic determination is in a much better agreement with the G3MP2B3 theory prediction of  $EA \approx 1.0$  eV [18].

To aid in the detailed analysis of the photoelectron spectrum, the geometries of both the neutral and anion species of glyoxal were optimized at the CCSD/aug-cc-pVTZ level, for both the C<sub>2v</sub> and C<sub>2h</sub> symmetry isomers. The optimized geometric parameters are included in Fig. 1 (in bold for the anion and in italics for the neutral). The calculated EAs and VDEs of the respective neutral and anion species are summarized in Table 1. The position of the 0 peak in the experimental spectrum (Fig. 2) matches well with the C<sub>2v</sub> EA value, but the experimental VDE is a better match for the corresponding C<sub>2h</sub> prediction. Clearly, additional analysis is required for a consistent interpretation of the data.

For both the anion and the neutral, the C<sub>2h</sub> structures are more stable than their C<sub>2v</sub> counterparts. Indeed, the previous studies established that the most stable structure of neutral glyoxal corresponds to the C<sub>2h</sub> isomer (Fig. 1, left), with a C<sub>2h</sub> to C<sub>2v</sub> internal rotation (isomerization) barrier of 2077 cm<sup>-1</sup> [27]. This barrier height is compared to the 1688 cm<sup>-1</sup> energy difference between the two isomers, determined by dispersed fluorescence spectroscopy [27] (or 1597 cm<sup>-1</sup> based on our calculations summarized in Fig. 1). The corresponding barrier height on the anion potential energy surface is not known. However, the electronic structure calculations described above indicate that the additional electron in the anion occupies an *a<sub>u</sub>* molecular orbital, which has a bonding  $\pi$  character with respect to the C–C bond. As a consequence, there is noticeable shortening of the C–C bond from neutral glyoxal to the anion (see Fig. 1). Given the additional (relative to the neutral)  $\pi$  bonding character, we infer that the internal-rotation barrier with respect to the C–C bond on the anion potential must be higher than that on the neutral. Therefore, the C<sub>2h</sub> to C<sub>2v</sub> isomerization should be less likely in the anion, compared to the neutral, and hence the dominant isomer of the anions generated by electron attachment to C<sub>2h</sub> glyoxal molecules should follow the same C<sub>2h</sub> structural motif.

The photoelectron spectrum expected in the photodetachment of the C<sub>2h</sub> anion was simulated using the PESCAL program [42,43]. The energy of the 0-0 photodetachment transition was set to 1.10 eV, matching peak 0 in Fig. 2 and the starting *ab initio* anion geometry shown in Fig. 1 (left) was adjusted to match the experimental spectrum (band A). The adjustment was done by treating the displacements along the neutral normal modes as adjustable parameters in order to match the final FC simulation to the experimental spectrum. In the process, the calculated FC intensities were multiplied by an  $eKE^{3/2}$  pre-factor, accounting for the Wigner-like [44] scaling of the electronic part of the photodetachment cross-section [45]. The scaled FC stick spectrum is

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