Anion photoelectron imaging spectroscopy of glyoxal

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A B S T R A C T

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 ± 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 ± 0.04 eV. The reported EA and VDE values are attributed to the most stable (C\textsubscript{2v} symmetry) isomers of the neutral and the anion.

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 ± 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 OHCCCHO forms two CHO radicals [28], while most famous is the ‘triple whammy’ dissociation into two CO molecules and H\textsubscript{2} [29].

Theoretical evidence from the previous as well as present work clearly shows that the C\textsubscript{2v} 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\textsubscript{2v} species is implied. The height of the internal rotation barrier between the C\textsubscript{2h} and C\textsubscript{2v} neutral isomers was investigated experimentally, with the results varying from 1770 ± 60 cm\textsuperscript{-1} by From During, Bucy and Cole in 1975 [32] to 2077 cm\textsuperscript{-1} by Butz in 1990 [27] (all values are with respect to the C\textsubscript{2h} minimum). Theoretical predictions of the barrier height vary from 1960 cm\textsuperscript{-1}, as determined by Scuseria and Schaefer in 1989 [30], to 2400 cm\textsuperscript{-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
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 N2O 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 ~106 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° 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 quality (aug-cc-pVTZ) were performed for both the anion and neutral species of glyoxal, yielding both the C2h and C2v, 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 (C2h or C2v). 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 X1A− − X1A− p photodetachment transition in the radical-anion of glyoxal (C2h isomer). The anion VDE is defined approximately by the position of the overall band A maximum. It was determined as VDE = 1.30 ± 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 ± 0.02 eV. This directly determined value is significantly different from the previous indirectly obtained result EA = 0.62 ± 0.26 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 = 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 C2v and C2h 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 C2v EA value, but the experimental VDE is a better match for the corresponding C2h prediction. Clearly, additional analysis is required for a consistent interpretation of the data.

For both the anion and the neutral, the C2v structures are more stable than their C2h counterparts. Indeed, the previous studies established that the most stable structure of neutral glyoxal corresponds to the C2v isomer (Fig. 1, left), with a C2v to C2h internal rotation (isomerization) barrier of 2077 cm−1 [27]. This barrier height is compared to the 1688 cm−1 energy difference between the two isomers, determined by dispersed fluorescence spectroscopy [27] (or 1597 cm−1 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 aπ molecular orbital, which has a bonding π 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) π 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 C2h to C2v 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 C2h glyoxal molecules should follow the same C2h structural motif.

The photoelectron spectrum expected in the photodetachment of the C2v 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 eKE3/2 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...
The stick spectrum was convoluted with an instrumental resolution function. The convolution was carried out in the speed domain and the resolution function was taken to be a Gaussian of a FWHM = 2 C2 104 m/s, as determined from O/C0 photodetachment under similar experimental conditions. The convoluted spectrum was then transformed into the eBE domain using the appropriate Jacobian. The result is shown in Fig. 2 in purple, overlaid with the experimental spectrum.

The agreement between the FC simulation and the experimental spectrum leaves little doubt about the robustness of the adjusted geometric parameters of the glyoxal anion included in Fig. 2. A similar simulation was attempted for the C2v anion isomer, but it failed to reproduce the observed spectral features, providing additional confirmation that the data in Fig. 2 (band A) do indeed correspond to the C2h isomer of the anion.

The minor feature, band B appearing as a broad low-eBE tail in the spectrum, cannot be accounted for by one-photon detachment of the glyoxal anion. Possible explanations for it include: hot bands, a two-photon process, or a coincident mass-to-charge species. The feature extending more than half an electron-volt below the EA is unlikely to be a hot band. A two-photon process is possible, but the signal intensity was insufficient to determine band A's scaling with laser power.

In the absence of conclusive proof, the most plausible explanation seems to be that band B corresponds to a coincident species with the same mass-to-charge ratio as the glyoxal anion, m/z = 58. The most likely candidate is the solvated anion of methylene, CH2C0N2O. In preparation of the glyoxal sample, methanol was used to extract the dehydrated solution from the sieve mixture (see Section 2). The methylene anion could be produced from the residual methanol present in the sample. Supporting this hypothesis, an m/z = 31 species, corresponding to the methoxide anion (CH3O ·), was also observed in the primary ion mass-spectrum, as was m/z = 75 (CH3O ·N2O). The electron affinity of CH2 is 0.652 eV [46], while the solvation energy by N2O is expected to be ~0.2 eV, making the CH2N2O cluster anion, whose mass is

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1 For interpretation of color in Fig. 1, the reader is referred to the web version of this article.
nominally coincident with that of glyoxal, a viable candidate for the origin of the weak B band observed in Fig. 2.

4. Summary

Using photoelectron imaging spectroscopy, we have measured the photoelectron spectrum of the glyoxal anion and obtained the first direct spectroscopic determination of the adiabatic electron affinity of glyoxal, $E_A = 1.10 \pm 0.02 \text{ eV}$. This result represents a significant revision of the indirectly determined value presently cited in databases. The vertical detachment energy of the radical-anion of glyoxal is determined as $VDE = 1.30 \pm 0.04 \text{ eV}$. These values are attributed to the most stable ($C_{2v}$) isomers of the neutral and the anion. Franck-Condon simulations indicate several vibrational modes activated upon electron photodetachment and successfully reproduce the observed spectral features. Future studies will examine the effects of substituents on the electron-binding properties of the molecule.

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