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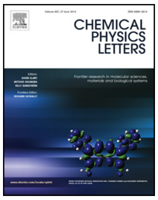

Infrared spectroscopy of the glyoxal radical cation: The charge dependence of internal rotation

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ABSTRACT

Glyoxal radical cations are produced in a pulsed discharge/supersonic molecular beam source. These ions are argon tagged and studied with mass-selected infrared laser photodissociation spectroscopy in the 1500–3500 cm^{-1} region. Five vibrational resonances are detected, three of which are assigned to two CH stretches and the asymmetric CO stretch fundamentals. Additional bands are assigned to vibrational combinations based on anharmonic frequency calculations. DFT calculations of the internal rotation coordinate, and the comparison of the predicted versus experimental IR spectra, show that the radical cation has only one stable structure, the trans conformer.

1. Introduction

Cis–trans isomerization plays an important role not only in organic chemistry but also in biochemistry [1]. The physical and chemical properties as well as physiological activity of a molecule strongly depend on its particular configuration. Internal rotation barriers can vary from non-existent (so-called free internal rotation) to several thousand wavenumbers. In the latter case, a clear distinction between two conformers can be made. However, in the case of barrierless or low-barrier rotations one often refers to internal rotational energy levels to account for the dynamical structure in high resolution spectra. There are many examples of internal rotations in molecules, some of which show identical limiting case structures due to the permutation of identical nuclei. One example is ethane, where rotation about the C—C bond transforms two identical structures into each other. The internal rotation leads to perturbations and splittings in the vibration–rotation–torsion energy levels [2]. These effects are present not only for the rotation of covalent bonds, but have also been shown for molecular complexes, e.g., benzene:water [3] and ammonium cation:water [4]. Internal rotation is well studied for neutral molecules and complexes, but little is known about ions. In the present work we investigate the torsional behavior upon ionization in the glyoxal cation.

Neutral glyoxal exhibits cis–trans isomerization, and both experimental and theoretical studies have investigated this molecule [5–16]. Most of the theoretical work focused on the potential energy surface along the torsional mode. One particular study investigated the ability of glyoxal to function as a molecular switch, changing conformation from trans to cis in the presence of strong electric fields [14]. Microwave and infrared spectroscopic methods have examined the ground state of glyoxal [6,9,10,15], while there are also several studies of its electronic states and photochemistry [15,17–19]. The trans conformer is lower in energy than the cis, however, small amounts of the cis isomer have been observed in the gas phase [6]. The energy difference between the two conformers and the isomerization barriers have been determined experimentally by Parmenter and coworkers by fitting observed energies for the torsional vibration in both conformers [10]. They reported an energy difference of 1688 cm^{-1}, a cis → trans barrier of 389 cm^{-1} and a trans → cis barrier of 2077 cm^{-1}. Whereas some glyoxal derivatives (in particular methyl glyoxal) have been investigated [17,20], there is only limited information on the cis–trans isomerization of the glyoxal cation. The isomers of $C_2O_2H_2^+$, of which glyoxal is only one example, have been investigated by ab initio calculations [16]. Portwood et al. concluded from an ESR study that the glyoxal cation exists primarily in the trans conformation [21]. They speculated that the cis conformation might become stabilized by a bonding interaction between the two oxygen atoms.

In the present work, the potential energy surface of glyoxal cation is investigated via infrared laser photodissociation spectroscopy and quantum chemical calculations. Our results indicate

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that the glyoxal radical cation is only stable in the trans conformation.

2. Experimental

Glyoxal cations are produced via electrical discharge in a pulsed supersonic molecular beam, as described previously [22–26]. The ambient vapor above a solution of 30% glyoxal in water (Sigma Aldrich) was added into a buffer gas flow containing 30% hydrogen and 70% argon. After the molecular beam is skimmed into the second chamber, ions are pulse-extracted into a reflectron time-of-flight mass spectrometer [27]. The ions of interest are mass selected and then intersected with the tunable output of an infrared OPO/OPA laser system at the turning point of the reflectron. Because infrared energies are not sufficient to break covalent bonds, we employ the argon-tagging technique [22–26]. Spectral intensities are not corrected for the laser pulse energy because of the variation in laser spot size/shape and thus its overlap with the ion beam in different wavelength regions.

Density functional theory (DFT) calculations are employed to investigate the electronic structure, potential energy surface (PES), and vibrational frequencies of the glyoxal cation using the GAUSSIAN 09 program package [28]. Harmonic as well as anharmonic (VPT2) frequency calculations at the B3LYP-D3/aug-cc-pVTZ level of theory were used to assign the experimentally observed IR spectral features. Relaxed PES scans of the torsional mode of neutral glyoxal, as well as its radical cation, were obtained by changing the torsional angle stepwise and allowing all other coordinates to relax. The PES scan was conducted at the B3LYP-D3/aug-cc-pVTZ level of theory. The structures, spectra, and PES of the neutral species were investigated for comparison with previous studies to validate these methods.

3. Results and discussion

The black trace (third from the top) in Figure 1 shows the experimental infrared spectrum measured for the glyoxal$^+$Ar cation in the mass channel corresponding to the elimination of argon. It consists of a single band at 1791 cm^{-1} near where the carbonyl stretch vibration is expected, two bands at 2822 and 2876 cm^{-1} in the higher frequency region where the C—H stretches are expected, and two weaker bands at 3076 and 3320 cm^{-1}. The 1791 cm^{-1} band has a poorer signal level, most likely because the laser power is about 10× lower here than it is near 2800 cm^{-1}. It is also conceivable that the dissociation yield is smaller here because of the lower photon energy, which is likely close to the argon binding energy. This 1791 cm^{-1} band can be compared to the asymmetric carbonyl stretch of neutral (trans) glyoxal at 1732 cm^{-1} [29]. The C—H stretch doublet at 2822/2876 cm^{-1} can be compared to the asymmetric C—H stretch of neutral (trans) glyoxal at 2835 cm^{-1} [29]. The other IR-active fundamentals of neutral glyoxal occur at frequencies lower than those covered by this experiment [29]. Neutral glyoxal does not have any fundamentals at frequencies higher than 2835 cm^{-1} where our two additional bands appear. The isolated glyoxal cation in the trans structure should have one IR-active C—H stretch, whereas the cis structure would have two (symmetric and asymmetric motions of the two CH groups). The two bands near 2800 cm^{-1} might therefore suggest that we have the cis isomer. However, the cis glyoxal cation should also have two IR-active carbonyl stretches (symmetric and asymmetric motions of the two carbonyl groups), and we see only one band here, consistent with expectations for the trans structure. We must also remember that the cation here is tagged with argon, and that the argon binding may introduce more asymmetry in the structure and additional bands in the spectrum. Therefore, we need theory for the cation, both with and without the argon, to be able to assign this spectrum.

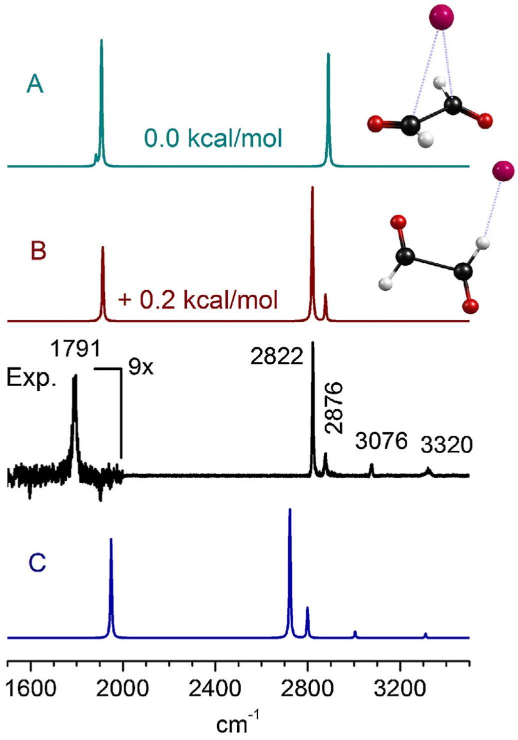

Figure 1. Experimental spectrum in black alongside scaled (0.968) harmonic frequencies for the two stable glyoxal:argon complexes as well as the anharmonic (VPT2) spectrum (blue, lower trace) for the 1H-bound conformer. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

To further investigate this system, computational studies were conducted at the B3LYP-D3/aug-cc-pVTZ level of theory on the neutral glyoxal molecule, and then on the glyoxal cation, in both the cis and trans structures for each conformer. The dispersion-corrected functional gave better results for the known cis–trans barrier in neutral glyoxal and is therefore used throughout these studies. Calculations on the cation also were done including the argon tag atom. These results are summarized in the Supporting Information. The computational results find the known stable structures for the cis and trans isomers of the neutral glyoxal, with the trans structure more stable, consistent with previous work [5–16]. The energy difference between the two conformers is calculated to be 1625 cm^{-1} (including only the torsional zero point energy). If all vibrational degrees of freedom are included in the ZPVE correction, the difference in energy is 1559 cm^{-1}. The scaled harmonic frequencies for the carbonyl stretch and asymmetric C—H stretch (1737 and 2841 cm^{-1}, respectively) are in nice agreement with the values known for the trans neutral from experiments (1732 and 2835 cm^{-1} [29]), validating this level of theory. A stable trans configuration is also found for the glyoxal cation, with a structure qualitatively similar to that of the corresponding neutral. However, we find no stable minimum for the cis cation structure. This was confirmed by harmonic frequency calculations, which show an imaginary frequency connected to the torsional mode. The trans cation structure is analogous to that of the neutral, but its bond distances and angles are quite different, as shown in Figure 2. In particular, the C—C bond distance is much longer in the cation, and the C—O bond distances are shorter. The H—C—O bond angle is much greater in the cation than it is in the neutral. Argon bonding in the tagged complexes does not affect these cation structural parameters significantly.