trans- and *cis*-Glyoxal: A Green's Function Calculation on Their Photoelectron Spectra

W. von Niessen

Contribution from the Lehrstuhl für Theoretische Chemie, Technische Universität München, D-8 München 2, West Germany. *Received April 21, 1977*

Abstract: The vertical valence ionization potentials of *trans*- and *cis*-glyoxal have been computed by a many-body Green's function method. For *trans*-glyoxal the experimental spectrum can be analyzed and the bands assigned. The agreement with experiment is very satisfactory. The ionization potentials of *cis*-glyoxal are predicted. The ordering of the ionization potentials is for *trans*-glyoxal: $5a_g(n_+)$, $4b_u(n_-)$, $1b_g(\pi)$, $1a_u(\pi)$, $4a_g$, $3b_u$, $3a_g$, $2b_u$ and for *cis*-glyoxal $5a_1(n_+)$, $4b_2(n_-)$, $1a_2(\pi)$, $1b_1(\pi)$, $3b_2$, $4a_1$, $3a_1$, $2b_2$, where n_+ and n_- denote the lone pair orbitals on the O atoms.

Introduction

Spectroscopic investigations have demonstrated that the preferred conformation of the glyoxal molecule is the planar trans structure.[1-3] A few years ago, however, a second conformer was identified and shown to be the planar cis form of glyoxal.[4-8] As the simplest dicarbonyl, *trans*-glyoxal has been the subject of a number of experimental and theoretical investigations, whereas fairly little is known about *cis*-glyoxal. The recent paper by Dykstra and Schaefer gives a short summary and a number of useful references.[9] To these references should be added the article by Leclerq et al.[10] These authors performed CNDO/S type calculations supplemented by configuration interaction on excited states of glyoxal. The photoelectron spectrum (PES) of *trans*-glyoxal has been recorded by Turner et al.[11] These authors assigned the first four bands in the spectrum to the $a_g(n_+)$,$b_u(n_-)$, $b_g(\pi)$, and $a_u(\pi)$ ionization potentials (IP's) (with increasing binding energy). Here n_+ and n_- denote the lone pair orbitals on the O atoms, which are symmetric and antisymmetric with respect to rotation about the twofold axis in the molecule. A fairly large splitting of about 1.6 eV is found between the $a_g(n_+)$ and $b_u(n_-)$ IP's. This large splitting is also found from some semiempirical[12,13] and ab initio calculations.[9] It has been explained in the perturbational model of through-space and through-bond interactions[14] as resulting from through-bond interactions, i.e., from a mixing of the lone pair orbitals, which are a priori assumed to be localized, with the σ-orbitals of the molecule.[12] Further on, the splitting appears to be nearly independent of the rotation angle about the C–C bond which transforms *trans*- into *cis*-glyoxal and vice versa.[13]

Turner's assignment of the PES did not remain undisputed. The semiempirical calculations of Kato et al. gave the ordering n,π,n,σ,π for both *trans*- and *cis*-glyoxal.[15] Ab initio calculations with basis sets of double-ζ or sub-double-ζ quality prefer the ordering n,π,n,π.[9,16,17] This is also the result of the most accurate calculation performed so far on these molecules by Dykstra and Schaefer.[9] It should be noted, however, that the first π- and the second n-orbital (from the ionization limit) are quite close together both for *trans*- and *cis*-glyoxal.[9] All the theoretical studies are based on Koopmans' theorem;[18] i.e., they neglect the influence of electron correlation and reorganization on the values of the IP's. Since further on polarization functions have not been included in any of these studies, the assignment of the PES of *trans*-glyoxal is still an open question.

In the present work theoretical calculations of the vertical valence IP's of both *trans*- and *cis*-glyoxal are reported which permit an assignment of the PES of *trans*-glyoxal. The IP's of *cis*-glyoxal are accurate predictions. The calculations go beyond Koopmans' theorem and include the effect of electron correlation and reorganization via a many-body Green's function method.[19] The subsequent section contains the results of the calculations.

Ionization Potentials of *trans*- and *cis*-Glyoxal

For the calculations the experimental geometries as determined for *trans*-glyoxal by Kuchitsu et al.[3] (see also ref 20) and for *cis*-glyoxal by Cole et al.[8] have been employed. The ab initio SCF calculations have been performed with the program system MUNICH of Diercksen and Kraemer.[21] The molecular orbitals (MO's) are expanded in Cartesian Gaussian functions. The basis set is C: (9s5p1d/4s2p1d); O: (9s5p1d/4s2p1d); H: (4s/2s). Calculations have also been performed without the polarization functions. The exponential parameters and contraction coefficients of the s- and p-type functions are taken from the work of Huzinaga.[22] The exponential parameters of the polarization functions are $\alpha_d(C) = 0.6$ and $\alpha_d(O) = 0.8$. The orbital energies and total SCF energies are listed for both molecules in Table I for the calculation with the polarization functions included.

The energetic ordering of the MO's is different from all previous ab initio calculations both for *trans*- and *cis*-glyoxal. From the ionization limit the ordering is for *trans*-glyoxal $a_g(n_+)$, $b_u(n_-)$, $b_g(\pi)$, $a_u(\pi)$ and for *cis*-glyoxal $a_1(n_+)$, $b_2(n_-)$, $a_2(\pi)$, $b_1(\pi)$. This result is obtained both for the basis set including polarization functions and without them. This result may appear somewhat surprising as Dykstra and Schaefer[9] used essentially the same basis set and obtained the ordering n,π,n,π of the MO's. However, there are two differences: a slightly different geometry is used here and another contraction scheme. Only little can be concluded from this difference in the orbital ordering. In the work of ref 9 and in the present calculation the second n- and the first π-type orbital are very close together in energy. This is also the case for the calculation with polarization functions. Even from this latter calculation it cannot be decided what the orbital ordering would be in the Hartree–Fock limit. All basis sets are too small to allow a conclusion to be drawn in this case. If two orbital energies are so close together as this pair it does not require great differences in electronic correlation and reorganization energy to change the ordering of states. A theoretical assignment of the PES of *trans*- and *cis*-glyoxal should thus include the effect of electronic correlation and reorganization to be reliable and have predictive capability for the spectrum of *cis*-glyoxal.

The Green's function calculations have been performed by including all 11 occupied valence orbitals and in the case of the calculations without polarization functions all and in the case of the calculations with polarization functions the 34 virtual orbitals of lowest orbital energy. Only the results obtained with the larger basis set are reported and discussed in detail. Es-

Table I. Orbital Energies (in eV) and Total SCF Energies (in a.u.) for *trans*- and *cis*-Glyoxal Calculated with Basis Set Including Polarization Functions[a]

trans-Glyoxal		*cis*-Glyoxal	
a_g	−561.00	a_1	−561.03
b_u	−561.00	b_2	−561.03
a_g	−309.94	a_1	−309.85
b_u	−309.93	b_2	−309.83
$1a_g$	−38.95	$1a_1$	−39.05
$1b_u$	−38.49	$1b_2$	−38.28
$2a_g$	−25.85	$2a_1$	−26.50
$2b_u$	−22.23	$2b_2$	−21.49
$3a_g$	−19.73	$3a_1$	−20.29
$3b_u$	−19.06	$4a_1$	−18.66
$4a_g$	−17.65	$3b_2$	−17.89
$1a_u(\pi)$	−16.21	$1b_1(\pi)$	−16.20
$1b_g(\pi)$	−14.47	$1a_2(\pi)$	−14.40
$4b_u(n_-)$	−14.12	$4b_2(n_-)$	−14.12
$5a_g(n_+)$	−12.12	$5a_1(n_+)$	−12.04
	Virtual Orbitals		
$2a_u(\pi)$	1.09	$2b_1(\pi)$	0.87
$5b_u$	4.91	$6a_1$	5.21
$2b_g(\pi)$	5.19	$2a_2(\pi)$	5.61
$6a_g$	5.98	$5b_2$	5.91
$6b_u$	7.16	$7a_1$	7.14
$7a_g$	9.81	$6b_2$	8.98
$3a_u(\pi)$	11.76	$3b_1(\pi)$	11.70
E_{tot}^{SCF} =	−226.546021 (−226.5182)[b]		−226.549234

[a] The numbering of the MO's starts with the first valence orbital.
[b] Reference 9.

Table II. Final Results for the Vertical Valence IP's of *trans*-Glyoxal

Symmetry	$-\epsilon_i$	$IP^{(2)}$	$IP^{(3)}$	$IP^{(R)}$	$P^{(R)}$	$IP^{(exp)}$
$5a_g(n_+)$	12.12	9.17	10.96	10.52	0.91	10.6
$4b_u(n_-)$	14.12	10.62	12.97	12.39	0.90	12.19
$1b_g(\pi)$	14.47	13.36	14.24	14.08	0.89	14.0
$1a_u(\pi)$	16.21	15.14	15.81	15.49	0.90	~15.4
$4a_g$	17.65	14.30	16.50	15.79	0.91	~15.9
$3b_u$	19.06	15.25	17.93	17.00	0.89	16.84
$3a_g$	19.73	16.89	18.13	17.50	0.88	>17.0
$2b_u$	22.23	19.70	20.43	20.02	0.88	—

sential differences between the calculations will be commented upon later. The results for *trans*-glyoxal are given in Table II and are plotted in Figure 1. Listed are the orbital energies, their symmetry identifications (C_{2h} point group), the results of the many-body calculations in second and third order of the perturbation expansion ($IP^{(2)}$, $IP^{(3)}$), the final results including the renormalization contribution ($IP^{(R)}$) together with the final pole strengths and the experimental maxima of the bands. Some of the IP's have been read off the published spectrum.[11] The determination of the maxima (or the centroids of the bands to which the computed IP's should be compared[23]) is rather difficult for the bands between 15 and 16.5 eV and between 16.5 and 17.5 eV, which both contain two IP's each as will be discussed below.

From Table II and Figure 1 it can be seen that Koopmans' theorem supplies the correct ordering of states; no change of ordering occurs in the final many-body calculations. It must be remembered, however, that different calculations produced different orderings and the use of Koopman's theorem could not supply a reliable prediction. The original assignment of Turner et al. of the PES of this molecule is thus the correct one. Koopmans' theorem supplies the correct ordering of states, but fails in the prediction of the spacings between the IP's. The $4b_u(n_-)$ IP and the $1b_g(\pi)$ IP are separated by 0.35 eV according to Koopmans' theorem but by 1.7 eV after the inclusion of many-body effects; the n-IP experiences a much larger shift than the π-IP. The latter value is in good agreement with the experimental value of 1.8 eV. The shifts from the Koopmans' values of the IP's introduced by the many-body calculations are rather nonuniform as is typically found for other molecules as well.[24] and vary between 0.4 and 2.2 eV. This sheds some light on the reliability of Koopmans' theorem for predictions in the case of close-lying bands (or even not close lying bands as in the present case).

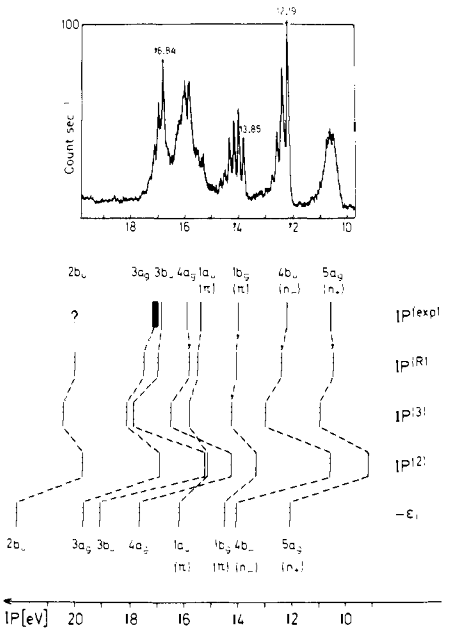

Figure 1. HeI photoelectron spectrum of *trans*-glyoxal (from ref 11) and ionization potentials calculated in different approximations.

The first band in the experimental spectrum arises from ejection of $5a_g(n_+)$ electrons, the second band from ionization of $4b_u(n_-)$ electrons, and the third band with the maximum at 14.0 eV from ionization of $1b_g(\pi)$ electrons. The band between 15 and 16.5 eV arises from two ionization processes as already noted by Turner.[11] One can estimate one maximum to be 15.4 eV or somewhat larger ($1a_u(\pi)$ IP) and a second one to be 15.9 eV ($4a_g$ IP). The band between 16.5 and 17.5 eV has not been analyzed by Turner. According to the calculations, two ionization processes give rise to this band. One maximum occurs at 16.84 eV ($3b_u$ IP), but the other one can hardly be estimated; one can only say that it occurs at values larger than 17 eV ($3a_g$ IP). The last computed IP is the $2b_u$ IP at 20.02 eV. The corresponding band cannot be seen in the HeI spectrum. The agreement of the computed IP's with the experimental values is very satisfactory in all cases and is rather typical for such basis sets as employed here.[24]

The Green's function calculations performed with the smaller basis set led to the same general conclusions. The quantitative agreement between the IP's computed with the two basis sets is very good for most of the IP's, but in three cases larger differences are found. The $1a_u(\pi)$, $3a_g$, and $2b_u$ IP's are larger by 0.2 to 0.3 eV when computed with the smaller basis set. The corresponding IP's ($1b_1(\pi)$, $3a_1$, $2b_2$) turn out to be larger by the same amount in the case of *cis*-glyoxal. For these IP's d-type functions must be regarded as essential to obtain quantitative agreement with experiment.

The results for *cis*-glyoxal are presented in Table III. The IP's of *cis*- and *trans*-glyoxal are plotted in Figure 2 (values according to Koopmans' theorem and the final results) to demonstrate the difference between the two molecules and the

Table III. Final Results for the Vertical Valence IP's of *cis*-Glyoxal

Symmetry	$-\epsilon_i$	$IP^{(2)}$	$IP^{(3)}$	$IP^{(R)}$	$P^{(R)}$
$5a_1(n_+)$	12.04	9.21	10.88	10.45	0.92
$4b_2(n_-)$	14.12	10.57	13.03	12.44	0.90
$1a_2(\pi)$	14.40	13.30	14.25	14.09	0.89
$1b_1(\pi)$	16.20	15.20	15.86	15.55	0.90
$3b_2$	17.89	14.48	16.74	15.99	0.90
$4a_1$	18.66	14.85	17.66	16.67	0.90
$3a_1$	20.29	17.44	18.66	18.08	0.87
$2b_2$	21.49	18.70	19.92	19.31	0.89

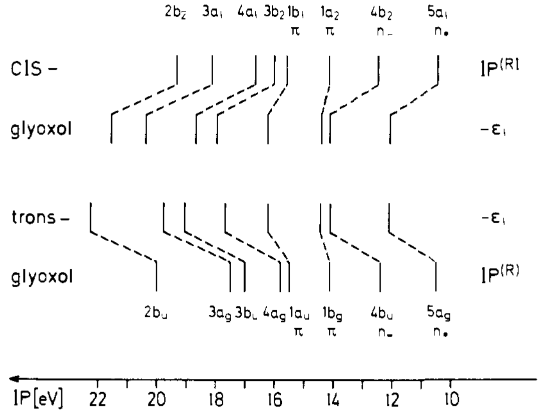

Figure 2. Ionization potentials of *cis*- and *trans*-glyoxal (values according to Koopmans' theorem and final results).

influence of many-body effects. Again only the data obtained with the larger basis set are given. Very similar features are found as has been discussed for *trans*-glyoxal. No change of ordering occurs from the ordering supplied by Koopmans' theorem. The $4b_2(n_-)$ and $1a_2(\pi)$ IP's are separated by 0.28 eV according to Koopmans' theorem and by 1.65 eV after the inclusion of many-body effects. The shifts introduced by the many-body calculations are again nonuniform and vary between 0.3 and 2.2 eV. The first four IP's of *cis*-glyoxal are the $5a_1(n_+)$, $4b_2(n_-)$, $1a_2(\pi)$, and $1b_1(\pi)$ IP's (listed with increasing binding energy). They are well separated. The fourth band will again be a band system arising from two ionization processes as has been found for *trans*-glyoxal. Ejection of $1b_1(\pi)$ electrons occurs at lower energy than ejection of $3b_2$ electrons. Note that in *trans*-glyoxal the $4a_g$ IP is smaller than the $3b_u$ IP, whereas in *cis*-glyoxal the $3b_2$ IP is smaller than the $4a_1$ IP. Whereas the fifth band system of *trans*-glyoxal arises from two ionization processes and is fairly narrow, the next two IP's of *cis*-glyoxal are fairly far apart (16.67 and 18.08 eV). The two bands are probably well separated except in the case of very extended vibrational progressions. The last computed IP of *cis*-glyoxal is the $2b_2$ IP at 19.3 eV.

A comparison of the IP's of *trans*- and *cis*-glyoxal is of interest. Cowan et al. found by extended Hückel type calculations that the n_+ and n_- IP's of *trans*- and *cis*-glyoxal are expected to be nearly equal.[13] This is also found in the ab initio calculations of ref 9 and in the present work. Moreover, it is found that the first four IP's agree to within 0.1 eV between the two molecules, whereas the IP's at higher energy have different values. The difference in structure between *trans*- and *cis*-glyoxal displays itself in the values of the inner valence IP's but not of the outer valence IP's. This is quite different from the case of *trans*- and *cis*-difluorodiazene, where the outer valence IP's differ between the molecules and the inner valence IP's are very similar.[25] No simple explanation is known for this behavior.

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