

fied PS 16 spectrometer from Perkin-Elmer Ltd (Beaconsfield, England); the accuracy is ± 0.03 eV for bands with vibrational fine structure and ± 0.05 eV for unresolved bands.

Compounds. The compounds were prepared using literature methods and purified by preparative gas chromatography. Identity and purity was confirmed by IR and NMR spectroscopy: 1,2-dimethylenecyclobutane (**3**) was obtained from *trans*-1,2-cyclobutanedicarboxylic acid by Cope elimination as reported by Doering and Dolbier;²⁴ 1,3-dimethylenecyclobutane (**4**) was obtained as described by Caserio and Roberts²⁵ from 3-methylenecyclobutanecarbonitrile²⁶ prepared from allene and acrylonitrile.

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On the Assignment of the Photoelectron Spectrum of *trans*-Oxalyl Fluoride

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Abstract: The ionization potentials of *trans*-oxalyl fluoride are computed by a many-body Green's function method. The ordering of the ionization potentials is according to the calculations: $7a_g(n_+)$, $6b_u(n_-)$, $2b_g(\pi)$, $2a_u(\pi)$, $6a_g$, $5b_u$, $5a_g$, $1b_g(\pi)$, $4b_u$, $1a_u(\pi)$. The computed splitting between the n_+ and n_- ionization potentials is 2.1 eV and between the first two π ionization potentials 0.5 eV.

I. Introduction

In a recent publication Frost et al.^{2a} presented the photoelectron spectra (PES) of the oxalyl halides (COX)₂ with X = F, Cl, and Br. The spectra were interpreted based on the assumption that the *trans* form of these molecules predominates in the gas phase. In fact the molecules can exist in *trans*, *cis*, and *gauche* forms and little is known at present about the equilibrium in the gas phase (see ref 2a for a summary and appropriate references). The PES in conjunction with variable temperature spectroscopy led to the conclusion that one form (probably the *trans* form) predominates in the gas phase, but other conformational isomers are present too. Based on calculations it was expected that two of the possible isomers have similar values of the ionization potentials (IPs) and that the third one differs in the IPs. Semiempirical calculations and the

known PES of related oxalyl compounds were taken as an aid in assigning the spectra. The assignment proved, however, to be a difficult task—in particular for oxalyl fluoride—because of the closely spaced bands and the complex and sometimes diffuse vibrational structure in the spectra. Thus only a tentative assignment was given for oxalyl fluoride and only certain bands were identified. Since this molecule is still small enough so that reasonably accurate calculations can be performed on it a theoretical assignment of the PES of this molecule will be given here. The IPs are calculated by an ab initio many-body Green's function method which includes the effect of electron correlation and reorganization.^{2b} This method has been successfully applied to a fairly large number of molecules and high accuracy can be achieved (see ref 3 and references cited therein). The results of these calculations are presented in the following section.

Table I. Orbital Energies (eV) and Total SCF Energy (au) for *trans*-(COF)₂^a

a _g	-718.34	1b _g (π)	-21.13
b _u	-718.34	5a _g	-20.78
a _g	-562.94	5b _u	-20.10
b _u	-562.94	6a _g	-18.40
a _g	-314.03	3a _u (π)	-17.04
b _u	-314.01	6b _u (n ₋)	-16.98
1a _g	-47.01	2b _g (π)	-16.21
1b _u	-46.66	7a _g (n ₊)	-14.64
2b _u	-41.68		
2a _g	-41.61	virtual orbitals	
3a _g	-28.45	3a _u (π)	0.225
3b _u	-24.61	3b _g (π)	5.29
4a _g	-23.61	7b _u	6.85
1a _u (π)	-22.08	8b _u	8.19
4b _u	-21.56	8a _g	8.23

$$E_{\text{tot}}^{\text{SCF}} = -424.069\ 320$$

^a The numbering of the orbitals starts with the first valence orbital.

II. Ionization Potentials of *trans*-Oxalyl Fluoride

The calculations have been performed at the experimental equilibrium geometry of *trans*-(COF)₂⁴ using the program system MUNICH⁵ to compute the SCF wave function. The basis set consists of Cartesian Gaussian functions and is of double- ζ quality. On each atom nine *s*-type and five *p*-type functions are used contracted to four *s*-type and two *p*-type functions with exponential parameters and contraction coefficients taken from the work of Huzinaga.⁶ The total SCF energy and the orbital energies are given in Table I. The notation n₊ and n₋ refers to the lone pair orbitals on the O atoms which are symmetric and antisymmetric with respect to a rotation about the twofold axis in the molecule. The notation n₊ and n₋ is only a very approximate one as basis functions on other atoms contribute to these molecular orbitals (MOs) as well.

It is seen from Table I that oxalyl fluoride possesses a fairly low-lying virtual orbital. This is an indication that considerable nonuniform many-body corrections can be expected and thus the ordering of ionic states obtained from Koopmans' theorem⁷ may not be the correct one. More precisely,^{8,9} for a linear or planar molecule the existence of a low-lying $\pi(\sigma)$ -type unoccupied orbital of nondiffuse character and of an outer valence $\pi(\sigma)$ -type occupied orbital leads to large many-body corrections for outer valence IPs of $\sigma(\pi)$ -type orbitals. The lowest virtual orbital of oxalyl fluoride is 3a_u(π) and there are outer valence occupied orbitals of π type, namely, 2b_g(π) and 2a_u(π). We therefore expect large Koopmans' defects for the 7a_g and 6b_u orbitals. Since the 6b_u orbital energy is only slightly lower than the 2b_g orbital energy an interchange of the ordering of the corresponding IPs is expected.

The Green's function calculations have been performed by including all 17 occupied valence orbitals and the 27 virtual orbitals lowest in orbital energy. Thus only 4 virtual orbitals have been left out of consideration except for the core orbitals. Their effect can only be a minor one (see ref 3). The results are given in Table II, which contains the following information: symmetry identification in C_{2h} symmetry, IPs according to Koopmans' theorem ($-\epsilon_i$), results in second and third order of the perturbation expansion (IP⁽²⁾, IP⁽³⁾), the renormalized final values (IP^(R)) and pole strengths (P^(R)), as well as the experimental values of Frost et al.^{2a}

As already expected Koopmans' theorem does not supply the correct ordering of states. According to Koopmans' theorem the 2b_g(π) IP is the second one and the 6b_u(n₋) IP is the third one from the ionization limit. Many-body effects, however, lead to an interchange of these two IPs. The energetic splitting between the 7a_g(n₊) and the 6b_u(n₋) IPs is 2.34 eV according to Koopmans' theorem and 2.07 eV in the many-body calculation. The corresponding splittings for the first two π IPs are 0.83 and 0.47 eV, respectively. The latter is surprisingly small when compared to *trans*-glyoxal. For *trans*-glyoxal the computed splittings between the n IPs are 2.0 (Koopmans' theorem) and 1.87 eV (many-body results), and between the π IPs 1.74 and 1.41 eV, respectively.¹⁰ The shifts in the IPs introduced by the many-body calculation vary from 1 to 2.5 eV.

Frost et al. assigned the first band in the PES to the 7a_g(n₊) IP in agreement with the present calculations. The next band system extends from 14 to 16.5 eV and was suggested to contain five IPs. The first part of this band between 14 and 15 eV was assigned to the 2b_g(π) IP at lower energy and the 6b_u(n₋) IP at higher energy. The principal argument was that in the reverse case the splitting between the 2b_g(π) and 2a_u(π) IPs would be too small. It was mentioned above that this splitting is exceptionally small for *trans*-oxalyl fluoride and the calculated ordering of the first three states is 7a_g(n₊), 6b_u(n₋), and 2b_g(π). The values of the next three measured IPs toward higher energy are 15.26, 15.55, and 15.97 eV. Then there is a gap until 17.05 eV. However, there is an important discrepancy here with the many-body calculations. One IP is definitely too many in this band system. The calculations place only four IPs in this energy range. Otherwise the 5b_u IP computed to be 17.63 eV would have to be assigned to the band at 15.97 eV, an error which is unacceptably large (see ref 3 for a discussion). It is difficult to decide which of the five bands which are clearly evident in the experimental spectrum does not arise from a simple ionization process. There exists the possibility that part of the structure in this extended band system is due to a rotational isomer. Calculations could be of help here, but without reliable geometries for the *cis* and the *gauche* forms of oxalyl fluoride, which are not yet available, there is little sense in performing these calculations. There is also the possibility of

Table II. Final Results for the Vertical Valence IPs of *trans*-(COF)₂ (eV)

symmetry	$-\epsilon_i$	IP ⁽²⁾	IP ⁽³⁾	IP ^(R)	P ^(R)	IP ^a (exp)
7a _g (n ₊)	14.64	11.48	13.09	12.63	0.91	12.63
6b _u (n ₋)	16.98	13.43	15.36	14.70	0.90	14.14 ^b
2b _g (π)	16.21	14.54	15.43	15.22	0.91	14.84 ^b
2a _u (π)	17.04	14.65	15.99	15.69	0.91	15.26 ^b
6a _g	18.40	14.39	16.69	15.98	0.92	15.55 ^b
						15.97 ^b
5b _u	20.10	15.86	18.46	17.63	0.91	17.05
5a _g	20.78	16.64	19.24	18.38	0.90	18.01
1b _g (π)	21.13	17.59	19.28	18.67	0.91	
4b _u	21.56	17.11	19.90	18.96	0.90	18.69
1a _u (π)	22.08	19.28	20.33	19.83	0.90	

^a Band maxima taken from ref 2a. The calculated values correspond to the centers of gravity of the bands. ^b In the energy range from 14 to 16 eV there can be only four IPs; one of the experimentally determined IPs has to be discarded (see text).

a complex band form due to vibrational excitations. In the absence of sufficient experimental information one can only state that only four IPs are to be assigned to the second band system and these are the $6b_u(n-)$ (14.70 eV), $2b_g(\pi)$ (15.22 eV), $2a_u(\pi)$ (15.69 eV), and $6a_g$ (15.98 eV) IPs. The CNDO-type calculations^{2a} lead, incidentally, to the same conclusion that only four IPs should be assigned to the second band system, but they do not lead to the same ordering of states. The $5b_u$ IP is to be assigned to the third band at 17.05 eV and the $5a_g$ IP to the sharp and intense fourth band at 18.01 eV. The last band discernible in the spectrum at 18.69 eV is associated with the $1b_g(\pi)$ and the $4b_u$ ips. The last π IP ($1a_u(\pi)$) is to be expected at 19.83 eV; i.e., both the $1b_g(\pi)$ and the $1a_u(\pi)$ IPs are found at considerably higher energies than initially expected. Since the lowest unoccupied orbital is of a_u symmetry and the highest occupied orbital of a_g symmetry one may expect low-lying poles of the self-energy part of a_u symmetry. If this is the case the calculated value of the $1a_u$ IP is unreliable and a different approach should be used.^{2b}

The theoretical calculations thus lead to a substantial revision of the assignment of the PES of *trans*-oxalyl fluoride. Assuming the extension of the basis set to be of minor impor-

tance for this molecule the ordering of ionic states can be unambiguously established. It also becomes apparent that more work on this molecule is required in order to elucidate the equilibrium among the various rotational isomers which can contribute to the bands in the PES and to determine their structures.

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Conformational Polymorphism. 2. Crystal Energetics by Computational Substitution. Further Evidence for the Sensitivity of the Method

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Abstract: The effect of crystal forces on molecular conformations has been investigated using a combination of experimental X-ray crystallography and theoretical lattice energy and ab initio calculations. We have extended techniques developed previously which take advantage of and rationalize the phenomena of conformational polymorphism—the existence of two or more crystal forms of the same molecule existing in significantly different conformations. Lattice energy calculations in conjunction with ab initio molecular orbital studies on the model compound *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline have been applied to answer the question as to why this molecule does not pack in a structure containing the ordered, low-energy, molecular conformation. The molecule was packed in the $P2_1$ lattice containing its dimethyl analogue. The lattice energy was minimized with three different potentials and the results were analyzed in terms of "partial atomic energy" contributions. All potentials showed the structure of the dichloro compound to be less stable than either the stable *Pccn* or metastable $P\bar{1}$ observed structures (by 1.5 and 2.5 kcal, respectively). The analysis in terms of the partial atomic energies showed the relative lack of stability to arise from the relatively unfavorable energetic environments of the aniline ring (including its Cl) as compared with its environment in the observed crystals. Finally comparison of the total energies (lattice plus intramolecular energy as obtained by molecular orbital calculations) accounted for the "observed nonexistence" of the low-energy conformation structure.

In the first paper in this series^{2a} we presented a newly developed technique for investigating the influence of crystal forces on molecular conformation. The phenomenon of conformational polymorphism is a particularly suitable basis for such studies since we take advantage of the fact that a flexible molecule may crystallize in polymorphic crystal forms in which the molecules adopt significantly different molecular conformations. If these conformations differ in energy, then the crystal forces must supply the energy to stabilize the more highly energetic molecular conformation. When the crystal structures differ between the polymorphs then the differences in the packing between the forms lead to these energy differences. For the crystal forms and molecules involved, the thorough investigation of these forces requires (1) full detailed crystal structure analyses to determine molecular geometries

and intermolecular relationships, (2) calculations of molecular energetics to obtain reliable estimates of the energetics of different molecular conformations, (3) lattice energy minimizations to obtain differences in crystal energies between the crystal forms, and (4) detailed analysis of the differences in packing and individual atomic contributions to the crystal energy to determine the particular crystal forces which stabilize one molecular conformation over another.

Such an analysis was previously carried out on the system *N*-(*p*-chlorobenzylidene)-*p*-chloroaniline (1). The material

