UV PHOTOELECTRON SPECTROSCOPY OF TRANSIENT SPECIES: GERMANIUM DIFLUORIDE (GeF_2)

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Received 14 April 1982; in final form 9 June 1982

The He(I) photoelectron spectrum of germanium difluoride (GeF_2) is reported. Results are analyzed on the basis of Hartree–Fock–Slater quantum-chemical calculations. A comparison is made with previous data for $GeCl_2$, $GeBr_2$, CF_2 and SiF_2.

1. Introduction

In UV photoelectron spectroscopy (PES) the obvious experimental difficulties encountered in the study of reactive short-lived gas-phase intermediates have been solved to a sufficient extent to make the method generally useful for the detailed study of the valence electronic structure of a variety of small molecules. In view of the importance of carbene reactions in synthetic chemistry unstable divalent halogenides of the group IVA elements have generated some interest. Application of the PE technique to SiF_2 [1,2] and CF_2 [3] has been reported. The carbene-like properties of the transient germanium dihalogenides have stimulated a recent study on $GeCl_2$ and $GeBr_2$ [4] where extensive use was made of a new method to produce these unstable species in the gas phase virtually free from unwanted side products. In a similar fashion, from the elevated temperature solid-state reaction between germanium monosulphide and lead difluoride almost pure germanium difluoride can be obtained in sufficient concentration to allow a PE study.

In spite of its transient character germanium difluoride has been known for a long time and various physical methods have been applied to this compound. Of the gas-phase studies we mention the molecular structure determination by means of microwave spectroscopy [5,6], the elucidation of the molecular vibrations using infrared spectroscopy [7,8] and the determination of the appearance potential with mass spectrometry [9]. In the present paper we describe the generation of GeF_2, its detection by means of PE spectroscopy and an analysis in terms of Hartree–Fock–Slater quantum-chemical calculations at the ab initio level.

2. Experimental

He(I) spectra of GeF_2 were recorded on a home-built microprocessor-controlled photoelectron spectrometer designed especially for the study of reactive short-lived species in the gas phase. In spite of these design measures which minimize the effects of deteriorating spectral resolution due to the gradual build-up of contamination on critical spectrometer surfaces, spectral drift during the course of the experiments still remains a problem. The limitation becomes all the more serious when multiscan operation is required, which is normally the case with the weak signals which the experimentalist encounters in dealing with transient species. However, the spectral drift problem can be effectively counteracted to a large extent by a "lock" procedure. An oven developed for solid-state reactions was employed and a gated detection method necessary to avoid interference with the heating current of the oven was used. Details of spectrometer construction, lock procedure, oven system and gated detection are given in previous papers [10–12].

In order to obtain GeF_2 in the gas phase virtually free from unwanted side products, the following solid-state reaction was employed:

$$GeS + PbF_2 \rightarrow PbS + GeF_2 \quad (\approx 300^\circ C).$$

Since the procedure is identical to the one used to obtain $GeCl_2$ and $GeBr_2$, we refer for more details to a previous paper [4].

The GeF_2 He(I) PE spectrum presented in fig. 1 was obtained with 57 scans of 25 s each. Spectra were run under conditions of ≈35 meV resolution on the $^2P_{3/2}$ argon band. Since a noble gas with bands which did not interfere with the GeF_2 spectra was not available, the first band of GeF_2 itself, or a suitable nitrogen PE band lying in a free spectral region were used as lock signals. The spectra were calibrated against the known ionization energies (IEs) of nitrogen, krypton and oxygen. No attempts were made to measure precise oven temperatures. The power input into the oven amounted to ≈7 W.

3. Results and discussion

As an important aid in the assignment of the GeF_2 PE spectrum Hartree–Fock–Slater (HFS) LCAO calculations were performed. In the HFS scheme the nonlocal exchange potential of the Hartree–Fock (HF) equations is replaced by a local exchange operator as proposed by Slater [13]. The resulting HFS equations are solved by the method of Baerends et al. [14]. IEs were determined using an extension of Slater's transition-state method which takes account of relaxation. In computing valence IEs all atomic cores were kept frozen.

The HFS calculations on GeF_2 were carried out using the microwave structure [6] with r(Ge–F) = 1.73209 Å and $\angle$(F–Ge–F) = 97.148°. Basis sets of triple-zeta Slater-type function (STF) quality were employed and no d-polarization functions were included. The molecules were oriented in the xz plane with the C_2 axis along z. Mulliken population analyses of the HFS LCAO ground state expressed in terms of AOs were utilized.

The general pattern of the valence PE spectrum of GeF_2 can be understood from simple MO considerations. As in $GeCl_2$ and $GeBr_2$ [4] interactions are expected between the fluorine 2p and the germanium 4s and 4p AOs. These fourteen valence electrons will give rise to seven bands in the He(I) PE spectrum, with two bands corresponding to out-of-plane and five to in-plane MOs.

In fig. 1 the He(I) spectrum of GeF_2 is presented. The rather sharp feature at 16.05 eV is due to an HF impurity apparently generated in the solid-state reaction. A number of low-intensity features at 11.05 eV (vertical IE, not shown) and at 12.8 and 13.5 eV (see fig. 1) always appear together but their dependence on experimental conditions differs from the behaviour of the bands assigned to GeF_2. Checks were made that these spurious bands could not arise from GeS, GeF_4 or PbF_2. However, ascribing these weak bands to the germanium difluoride dimer, especially in view of the appearance potential obtained for this compound [9], might not be unreasonable. The remaining features in the spectrum are ascribed to GeF_2. The first band has an adiabatic IE of ≈11.65 eV, in good agreement with a previously measured appearance potential for GeF_2^+ of 11.8 ± 0.1 eV [9]. No vibrational structure is resolved on this band. Since the progression on the first PE band of CF_2 is due to the symmetric bending vibration [3] and because the bending mode in neutral GeF_2 occurs at 263 cm^{-1} [7], the observed absence of structure in our PE spectrum is not surprising. The feature at 14.5 eV shows an intensity and a slight asymmetry suggestive of more than one PE band. Similarly the structure in the region between 15.5 and 16.1 eV indicates the precence of more than one photoionization phenomenon. Finally a rather weak band at 18.7 eV is found. On the basis of our HFS calcula-

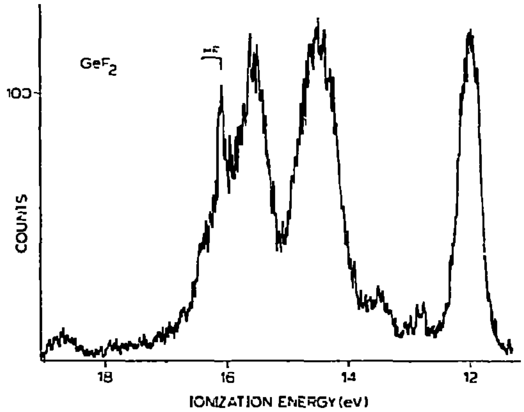

Fig. 1. He(I) photoelectron spectrum of GeF_2.

Table 1
Experimental IEs, results of HFS LCAO calculations for CF_2, SiF_2 (double zeta) and GeF_2 (triple zeta) and preferred spectral assignments (all values in eV). In addition experimental and calculated electric dipole moments are given

MO [a]	CF_2		SiF_2		GeF_2	
	HSF(DZ)	exp. [3]	HFS(DZ)	exp. [2]	HFS(TZ)	exp.
$4a_1$	12.60	12.27	10.84	11.18	11.30	11.98 ± 0.03
$3b_1$	17.20	16.4	14.60	15.5	13.54	14.4 ± 0.2
$1a_2$	17.81	17.4	15.30	15.8	13.87	14.4 ± 0.2
$3a_1$	19.03	19.2	15.60	16.8	14.46	15.55 ± 0.05
$1b_2$	19.68	20.8	15.99	17.06	14.44	15.9 ± 0.2
$2b_1$	20.54	22.2	16.44	17.8	15.05	16.2 ± 0.2
$2a_1$	23.20	24.0	18.30	–	17.62	18.70 ± 0.03
dipole (D)	0.39	0.46 [15]	1.71	1.28 [16]	2.75	2.61 [6]

[a] Valence orbital numbering.

tions and in view of the results obtained for the related compounds $GeCl_2$ and $GeBr_2$ [4] we assign two photoionization bands to the feature at 14.5 eV and three bands to the structure around 16 eV. Experimental band positions some of which are rather inaccurate due to spectral overlap are presented in table 1.

The results of the HFS calculations are also summarized in table 1. Our experience with these calculations applied to a variety of small molecules shows that although absolute IE values cannot be reproduced to better than ≈1 eV, relative band positions tend to be reliable to ≈0.3 eV. For PE bands which lie closer than ≈0.3 eV an assignment based on HFS calculations alone should be considered as tentative. In table 1 an HFS-based preferred spectral assignment (using the HFS valence orbital numbering) is presented. When an overall shift of 0.8 eV is applied to the calculated values good agreement with experiment is obtained. Also the calculated and experimental electric dipole moments for GeF_2 agree quite well.

In fig. 2 an almost self-explanatory pictorial representation of the orbital interaction scheme in GeF_2 is given. The pattern is based on interactions between the germanium 4s and 4p and fluorine 2p orbitals. The solid lines correspond to HFS results while the dotted lines are estimates of the atomic valence levels in the final molecular field. Interaction lines are only included when the AO contribution to the resulting MO exceeds 10%.

When the experimental PE band positions for GeF_2, $GeCl_2$ and $GeBr_2$ [4] are plotted against the first IEs of fluorine, chlorine and bromine atoms (17.42, 12.97 and 11.81 eV respectively) approximately linear correlations are obtained, thus providing confirmation for our assignments. The relatively gentle slopes of the $2a_1$ and $4a_1$ correlation lines are due to the significant germanium 4s participation in these orbitals, the steeper slopes of the remaining lines indicate predominant halogen character (see also fig. 2).

A correlation between the GeF_2 results and CF_2 [3] and SiF_2 [1,2] data can also be attempted by plotting the PE spectra against the bond distances between the fluorine and the central atom. In order to get more insight we have performed HFS calculations of double-zeta quality on CF_2 and SiF_2 on the basis of their microwave geometries [15,16]. The results of these calculations are summarized together with the experimental data in table 1. The calculations for SiF_2 are in reasonable agreement with the experimental values, while the agreement for CF_2 is worse.

The calculations show that in many ways the chemical bonding in these three different molecules is similar. In each PE spectrum we can distinguish a fluorine lone pair region defined by the $3b_1$ (100%), $1a_2$ (100%) and $3a_1$ (90%) ionization phenomena (see also fig. 2). While for GeF_2 and SiF_2 the $1b_2$ and $2b_1$ IEs are fairly close to this lone pair region, in CF_2 these two IEs are much more stabilized due to strong bonding interaction of the carbon 2p MOs with the fluorine 2p AO symmetry combinations. The location of the $4a_1$ and $2a_1$ IEs is, roughly speaking, determined by the interaction between the central atom valence s AO and the radial fluorine 2p combination of a_1 symme-

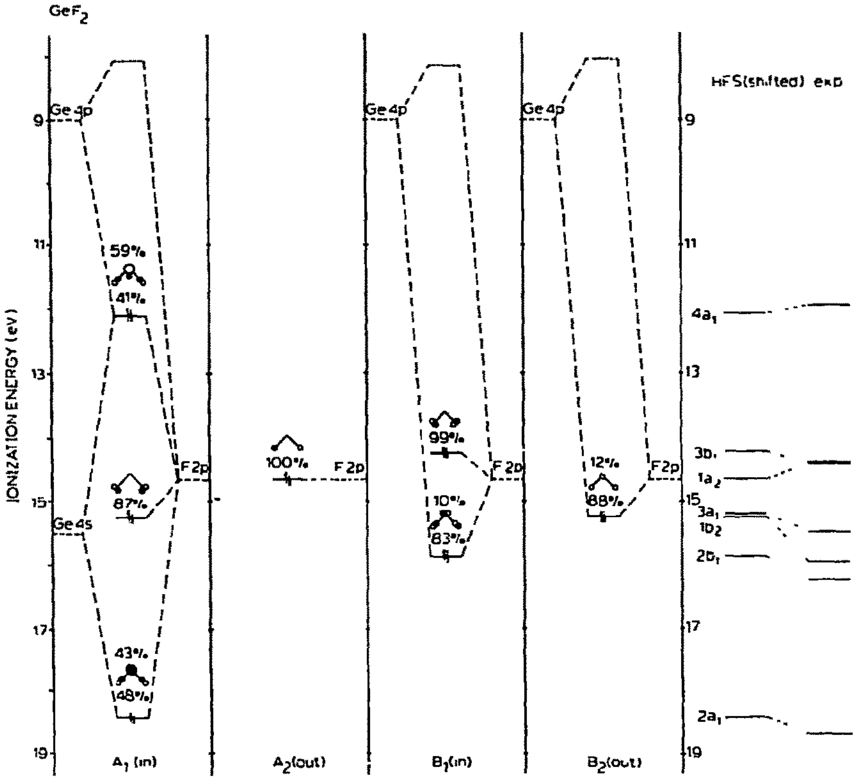

Fig. 2. Experimental IEs and orbital interaction scheme based on results of HFS LCAO calculations (shifted by 0.8 eV) for GeF_2.

try. This might explain the unusual trend observed in the position of the first bands ($4a_1$) in CF_2, SiF_2 and GeF_2 which is parallelled by the valence s orbital IEs of the free central atoms (19.5, 15.0, and 15.6 eV respectively [17]).

Moreover, the calculations show the trend towards ionic bonding character throughout this series of molecules, which is illustrated by the charges on the central atom, i.e. +0.5*e* (C), +1.0*e* (Si) and +1.1*e* (Ge). Also the contribution of the valence p AO of the central atom to the $4a_1$ MO is increased in going from germanium/silicon to carbon, in line with the well-known tendency of the carbon atom to form s–p hybrids.

Acknowledgement

One of the authors (GJ) wishes to acknowledge the Netherlands Organization for the Advancement of Pure Research (Z.W.O.) for financial support. The authors are grateful to a referee for helpful comments.

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