DEUTSCHES ELEKTRONEN-SYNCHROTRON DESY

VUV-Spectra of the Xenon Fluorides

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ABSTRACT

The absorption spectra of gaseous XeF_2, XeF_4, and XeF_6 have been
accurately measured in the photon energy range from 5 to 35 eV
with the use of the synchrotron radiation of DESY.
The vibrational structure of several Rydberg transitions could
be resolved. The spectra are interpreted and most of the struc-
tures could be assigned. From these data, information about the
ionized species is obtained. The assignment of the first two IP's
of XeF_4 is corrected.

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I. INTRODUCTION

Since the discovery of the stable xenon fluorides in 1962, many investigations, both experimental as well as theoretical, have been undertaken on these interesting molecules. They are by now known rather well, although there still exists some ambiguity concerning such fundamental properties as the ordering and assignment of the one-electron levels in the valence shell or, in the case of XeF_6, the geometry and ground state electronic configuration. Whereas some additional information on the latter problem could recently be obtained by far XUV absorption spectroscopy[1], near XUV spectroscopy may help to confirm or correct the assignment of some of the one-electron levels measured in photoelectron spectroscopic and photoionization mass spectrometric experiments[2-6].

Besides the high energy region above 40 eV[1,7], the optical spectra of the molecules are still known only below 11 eV for XeF_2[3,8-10] and XeF_4[9,11] and below 6 eV for XeF_6[12]. Furthermore these spectra are only of medium accuracy and resolution. Thus the Rydberg type fine structures converging to different ionization potentials could either not be detected or only poorly be resolved so that no safe interpretation was possible.

Therefore we have measured the spectra of XeF_2, XeF_4 and XeF_6 in the energy range from 6 to 35 eV with high resolution. Our far XUV results[7] were helpful in assigning the spectra. Even the vibronic structure of several bands could be resolved, from which information on the structure of the ionized species is obtainable.

II. EXPERIMENTAL SETUP

The experimental setup was similar so that used by Koch et al.[13]. The continuum of the synchrotron radiation of the Deutsches Elektronen-Synchrotron DESY was monochromatized by a one meter normal incidence monochromator[14]. Using a 2400 ℓ/mm Bausch & Lomb grating and an exit slit

of 100 μ width, a spectral bandwidth of about 1 $\overset{o}{A}$ was achieved over the whole energy range corresponding to a resolution of about 10 meV at 10 eV. The wavelength calibration was checked to be accurate within ± 1 $\overset{o}{A}$.

For the absorption measurements on the molecules in the gas phase a windowless all stainless steel absorption chamber of 1 m length was used. It was separated from the monochromator by a differential pumping system. The pressure in the chamber (in the order of 0.01 Torr) was controlled by a membrane vacuummeter. The light traversing the sample chamber hit a sodium salicylate layer on a glass window and was converted into 4100 $\overset{o}{A}$ light measured by a photomultiplier.

III. SUMMARY OF EXPERIMENTAL RESULTS

The measured absorption cross section curves for the free molecules XeF_2, XeF_4 and XeF_6 are shown in Fig.s 1,2,3. The spectra in the energy range from 0 to 35 eV may be divided into six regions:

Region 1: (forbidden valence transitions) - The weak tail of the spectrum below about 6 eV is not reproduced here. As known from the literature, there appear some very weak (f < 0.01) and broad maxima: (XeF_2: 5.3 eV, shoulder near $4^{1/2}$ eV; XeF_4: 4.8 and 5.4 eV, shoulder near $4^1/2$ eV; XeF_6: 3.6 eV, shoulder near 3 eV, shoulders between $4^1/2$ and 6 eV). Below the Rydberg type orbitals, these molecules possess only one empty orbital in the valence shell which consists mainly of the Xe 5p orbital (XeF_2: σ_u; XeF_4: e_u; XeF_6: t_{1u}[15]). As it is strongly antibonding, excitations into it will give rise to broad bands. The highest occupied MO's, correlated to Xe 5s and Xe 5p AO's, are of σ_g and π_u type (XeF_2), of a_{1g} and a_{2u} type (XeF_4), and of a_{1g} type (XeF_6[15]). The lowest energy transitions to be expected are therefore to the $^3\Pi_g$, $^3\Sigma_u^+$, $^1\Pi_g$ states of XeF_2, to the ^3E_g, ^3E_u, ^1E_g states of XeF_4 and to the stronlgy Jahn-Teller split $^3T_{1u}$ states of XeF_6. They are allowed only by vibronic and spin-orbit coupling[9b].

Region 2: (allowed valence transitions) — There remains one orbitally and spin allowed transition to a $^1\Sigma^+_u$, a ^1E_u, and a $^1T_{1u}$ state, respectively. This transition, together with excitations from lower lying gerade MO's (being composed of F 2p AO's) gives rise to strong broad humps at energies above 6 eV: at 7.85 eV (f = 0.5) for XeF_2, at 6.65 eV (f = 0.2) and 9.32 eV (f = 0.8) for XeF_4 and at 10.1 eV (f ~ $2^1/2$) with several shoulders on both sides of the maximum for XeF_6. The literature values for XeF_2 and XeF_4[8,9,11] differ only slightly from our values; in particular we could reproduce the low energy foot of the 9.3 eV band of XeF_4 at 8.4 eV, discussed by Basch et al.[15], as well as its high energy asymmetry (see Fig. 5).

Region 3: (Rydberg transitions) — At higher energies, excitations from the highest (slightly antibonding) MO's into the nonbonding Rydberg orbitals result in a series of sharp bands which converge to the lowest IP's of XeF_2 at 12.4, 12.9 and 13.6 eV, of XeF_4 at 13.1 and 13.4 eV, and of XeF_6 at 12.5 eV. Details on the highly resolved Rydberg spectra of XeF_2 and XeF_4 (see Figs. 4 and 5) and the corresponding ionization limits will be given in the next section.

Region 4: (complex transitions) — Above about 12 eV the structures in the spectra become broader and broader because of ionization and dissociation processes. In the case of XeF_2 the vibrational structure begins to be smeared out near 11.5 eV (Fig. 4), a value which agrees with the onset of the predissociation process $XeF_2 \rightarrow Xe^+ + F^- + F$[6]. Above the $^2\Pi_{u3/2,1/2}$ IP's at 12.4 and 12.9 eV, the direct ionization continuum is perturbed by several autoionization processes observed in a photoionization mass spectrometric study[6]. The asymmetric line profiles in Fig. 4 might be related to higher Rydberg excitations or stem from double excitations. No sharp structures are observable above the third IP (σ_g) of XeF_2 at $13^1/2$ eV, nor above the corresponding IP's of XeF_4 (second IP(a_{1g}) at $13^1/2$ eV) and XeF_6 (first IP (a_{1g}) at $12^1/2$ eV).

<u>Region 5</u>: (Xenon 5p ionization) - The 5p-photoionization cross section of the free xenon atom has a fairly high maximum of about 63 Mb slightly above the threshold and than goes down rather rapidly[16,17], whereas the other corresponding atomic photoionization cross sections (Xe 5s, F 2p, F 2s) exhibit only a weak energy dependence[17]. Therefore it seems natural to attribute the 14.0 eV peak of XeF_2 and the 14.2 eV peak of XeF_4 to the first ionization continuum from the XeF_2 π_u and the XeF_4 a_{2u} orbital. These species have a large Xe 5p population[15] and their vertial IP's are both $1^1/2$ eV below the peaks. XeF_6 has no low-lying MO with Xe 5p contribution[15]; therefore no comparable peak occurs in the XeF_6 spectrum. This corresponds to the low Xe 5p population in the XeF_6 molecule[15], which would be zero in the case of pure ionic binding: $Xe^{6+}(F^-)_6$.

<u>Region 6</u>: (higher ionization continua) - Ionization from the lower valence MO's leads to a series of overlapping continua with onsets at the IP's. The main feature is the broad intense hump with a long tail and a maximum near 23 eV in all three molecules. This hump is absent in xenon and becomes more and more intense on going to XeF_2, XeF_4 and XeF_6. It corresponds to the atomic F 2p ionization in intensity, which however shows a much flatter energy dependence[17]: The F-F-distance in these molecules is about 4 Å, free electrons with such a deBroglie wavelength (E_{kin} ~ 1o eV) optimally overlap with the molecular orbitals. This explains the pronounced maximum of the molecular cross section nearly 1o eV above the IP's.

IV. RYDBERG TRANSITIONS AND IONIZATION LIMITS IN XeF_2 and XeF_4

The Rydberg spectra are drawn on a larger scale in Fig. 4 (XeF_2) and Fig. 5 (XeF_4).

<u>Rydberg transitions in XeF_2</u>: The energies given by Brundle[3] for the maxima of the first two Rydberg transitions are confirmed by our measure-

ment ($\Delta E \simeq + 15$ meV), whereas the old values of Jortner[8,9a] for the
first four or five bands are too large ($\Lambda E \simeq + 150$ meV). Our assignment,
which differs from Jortner's, is also shown in Fig. 4. It is <u>consistent</u>
<u>with the IP's given in the literature</u>[2,3,6]. In the overlapping region
above 10.5 eV the assignment is not absolutely certain.

The most prominent features are the four $\pi_{u3/2}$, $\pi_{u1/2} \to$ ns, nd
Rydberg series. Furthermore there seems to exist a $\sigma_g \to$ np series. The
corresponding quantum defects δ are 4.1 (s), 3.8 (p) and 2.5 (d). These
values agree with our far XUV measurements[7], from which we conclude that
the p-series should be of π-type. The d-series are most probably of
δ-type.

The first two Rydberg bands $\pi_{u3/2,1/2} \to$ 6s are shown with maximum
resolution in Fig. 6. Ample vibrational structure can be seen. In its
linear ground state XeF_2 has three normal vibrations[18,19]: σ_g^+ symmetric
stretching ($v_1 = 63.8$ meV), σ_u^+ asymmetric stretching ($v_3 = 68.8$ meV), and
π_u binding ($v_2 = 26.4$ meV). The π_u orbital is nearly nonbonding but is ex-
pected to stabilize the linear geometry. Therefore it seems natural to
assume that after excitation of a π_u electron the molecule still remains
linear and symmetrical, with only slightly changed Xe-F bond length
(2.00 Å in the ground state), but with a significantly reduced bending for-
ce constant. With these assumptions it is possible to reproduce the measured
spectrum nearly exactly by fitting the vibrational constants of the final
state. The results are given in Table 1. The inherent line width of about
9 meV just agrees with the resolving power of our instrument. The absorption
lines are caused by excitation of the totally symmetric σ_g^+ stretching and
by the π_u bending vibration. Hot bands are also present. The main vibrational
contributions to the measured peaks are indicated in Fig. 6.

The remaining Rydberg structure is shown in Fig. 7. The next two peak
series correspond to the $\pi_u \to$5d excitations. Contrary to the $\pi_u \to$ 6s tran-
sitions, no v_2 progression is measurable. From this result it follows that
the bending force constant is not significantly weakened. Evidently the
$5d_\delta$ electron stabilizes the linear configuration. From Table 1 one can also
see a different behaviour of the $\pi_{3/2}$ and $\pi_{1/2}$ excited states:

$$v_1(\pi_{3/2}^*) > v_1 \text{ (ground state)} > v_1(\pi_{1/2}^*).$$

A corresponding trend seems to exist in the Xe-F bond lengths.

Combining our VUV and XUV-results[7] we obtain the following Rydberg orbital energies (Table 2).

Rydberg transitions in XeF_4: The Rydberg spectrum of XeF_4 is shown in Fig. 5. The orbital, corresponding to π_u in XeF_2, is the a_{2u} one. Excitation of an electron from it will not only reduce the out of plane bending force constant, but even seems to result in a non-planar equilibrium geometry of the excited molecule. Therefore the $a_{2u} \to ns$ Rydberg series consists of rather broad bands, the maxima of which converge to the first vertical ionization potential at 13.06 eV[4]. The quantum defect of the ns-orbitals is $\delta = 4.0$, in agreement with the far XUV result[7].

On the other hand, the 5d out-of-plane orbital is capable of stabilizing the planar geometry, similar to the situation in XeF_2. The corresponding band at 10.9 eV ($\delta = 2.5$) shows well resolved vibrational structure, which seems impossible to be assigned in the case of such a polyatomic molecule. However, it might be suggested that the doublet structure of about 0.06 eV occurring in this and the three other broader bands is caused by the totally symmetric vibration with v = 0.069 eV in the ground state[19].

The analog to the $\sigma_g \to 6p$ excitation in XeF_2 is the $a_{1g} \to 6p$ transition. As a $6pe_u$ orbital ($\delta = 3.5$) gives rise to a linear Jahn-Teller distortion in this non-linear molecule, we again obtain only a broad band.

So far the first two ionization potentials of XeF_4 have always been assigned in the literature[4,6,15] in an opposite manner: a_{1g} 13.1 eV, a_{2u} 13.4 eV. Nevertheless under this assumption it is absolutely impossible to assign our spectrum. Our revised assignment of the two IP's and the interpretation given above also explains much better the data mentioned in the literature:

1) Basch et al.[15] have performed limited basis SCF calculations on XeF_2, XeF_4, and XeF_6 and have obtained 12.78, 12.65, and 11.73 eV, respective-

ly, for the <u>first g-type vertical IP</u>. The experimental values for XeF_2 and XeF_6 are 13.65 and 12.51 eV [2-4], which is ~ 0.8 eV larger. Therefore the a_{1g} VIP of XeF_4 is expected to be 12.65 + 0.8 = 13.45 eV. The theoretical results for the <u>first u-type VIP</u> (semiempirically scaled according to Ref. 15) are 12.5 eV for $\pi_{u3/2,1/2}$ of XeF_2 and 13.1 eV for a_{2u} of XeF_4.

2) The interpretation of the absorption lines given above also explains why the width of the XeF_4 a_{2u} photoionization band is as large as 0.5 eV [4], although the a_{2u} orbital is expected to be nearly nonbonding [15], that is without influence on R_e (line width of the XeF_2 π_u ionization = 0.2 eV [2], ΔR_e < 5 %), whereas ionization from the slightly antibonding gerade orbital [15] leads to a width of not larger than 0.3 eV in both molecules [2,4]. We assume that the mentioned width of 0.5 eV is caused by angular distortion, not by bond lengthening.

3) This interpretation also easily explains the decomposition of XeF_4^+ into XeF_3^+ + F above 12.91 eV photon energy via excitation of the b_1 out of plane bending mode. This dissociation process has been measured by Berkowitz [6] et al., who could give no cinvincing explanation for it on the basis of the old assignment of the IP's.

Whereas our measurements gave information on the first few IP's, the values of the highest valence electron IP's of all three molecules are still in question. According to theoretical estimates [5,15], the higher a_{1g} Xe 5s-type IP's should lie in the range of 27 eV and not as low as proposed by Brundle [4]; (then the $4a_{2u}$ and 6_{eu} IP's of XeF_4 too would have to be revised, probably: $6e_u$ = 17.9, 18.4 eV and $4a_{2u}$ = 19.8 eV). Further investigations are necessary on this problem.

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Figure Captions

Fig. 1:   Absorption cross section of gaseous XeF_2 at room temperature
           (1 arbitrary unit corresponds to 1 Mb ±20 %) vs. photon energy
           from 6 to 34 eV. The vertical ionization potentials are also
           given on the abscissa.

Fig. 2:   Absorption cross section of gaseous XeF_4 at room temperature
           (1 arbitrary unit corresponds to 1 Mb ± 20 %) vs. photon energy
           from 6 to 34 eV. The vertical ionization potentials are also
           given on the abscissa.

Fig. 3:   Absorption cross section of gaseous XeF_6 at room temperature
           (1 arbitrary unit corresponds to 1 Mb ± 30 %) vs. photon energy
           from 6 to 34 eV. The vertical ionization potentials are also
           given on the abscissa.

Fig. 4:   Rydberg spectrum of gaseous XeF_2.

Fig. 5:   Rydberg spectrum of gaseous XeF_4.

Fig. 6:   Vibrational structure in the Rydberg transitions $\pi_{3/2,1/2} \rightarrow 6s$
           of XeF_2. The numbers in parenthesis denote the vibrational
           transitions $n_1'' \, n_2'' \rightarrow n_1' \, n_2'$.

Fig. 7:   Rydberg spectrum of XeF_2 in the energy range from 10 to 12.5 eV.
           The vibrational structure is indicated by lines, the bold ones
           corresponding to the 0-0 transition.

Table 1:   Spectroscopic constants of XeF_2

	ground state	$\pi_{3/2} \to 6s$	$\pi_{3/2} \to 7s,8s$	$\pi_{3/2} \to 5d$	$\pi_{3/2} \to 6d$	$\pi_{1/2} \to 6s$	$\pi_{1/2} \to 5d$
v_1 (meV)	63.8	66 ± 1	65 ± 1	65 ± 1	60 ± 5	62 ± 2	60 ± 3
v_2 (meV)	26.4	9 ± 1		~25		13 ± 1	~ 25
$|\Delta R|$ (mÅ)	– 0 –	50 ± 5	50 ± 5	60 ± 5	55 ±10	25 ± 3	35 ± 5

Table 2:   Rydberg orbital energies of XeF_2

Rydberg orbital	energy (eV)
6s	− 3.75
6pπ	− 2.75
6pσ	− 2.45
5d (δ)	− 2.25
7s	− 1.7
7pπ	− 1.4
7pσ	− 1.2
6d (δ)	− 1.15
8s	− 0.9

Fig. 1

XeF₂ (gas) absorption cross section vs photon energy. Labeled features at 7.85, 8.58, 9.14, 10.07, 10.70, 11.16, 11.49, 11.95, 12.29, 14.0, 14.9, 16.6, 17.5, and 23.5 eV. Axes: ABSORPTION CROSS SECTION (arb.units) from 40 to 160, and PHOTON ENERGY (eV) from 5 to 35. Orbital labels: π_u, σ_g, π_g, π_u, σ_u.

XeF₄ (gas)

Fig. 2

XeF_6 (gas)

ABSORPTION CROSS SECTION (arbitrary units)

PHOTON ENERGY (eV)

10.10
10.50
10.90
11.25
11.49
12.55
13.30
14.25
15.10

12.35

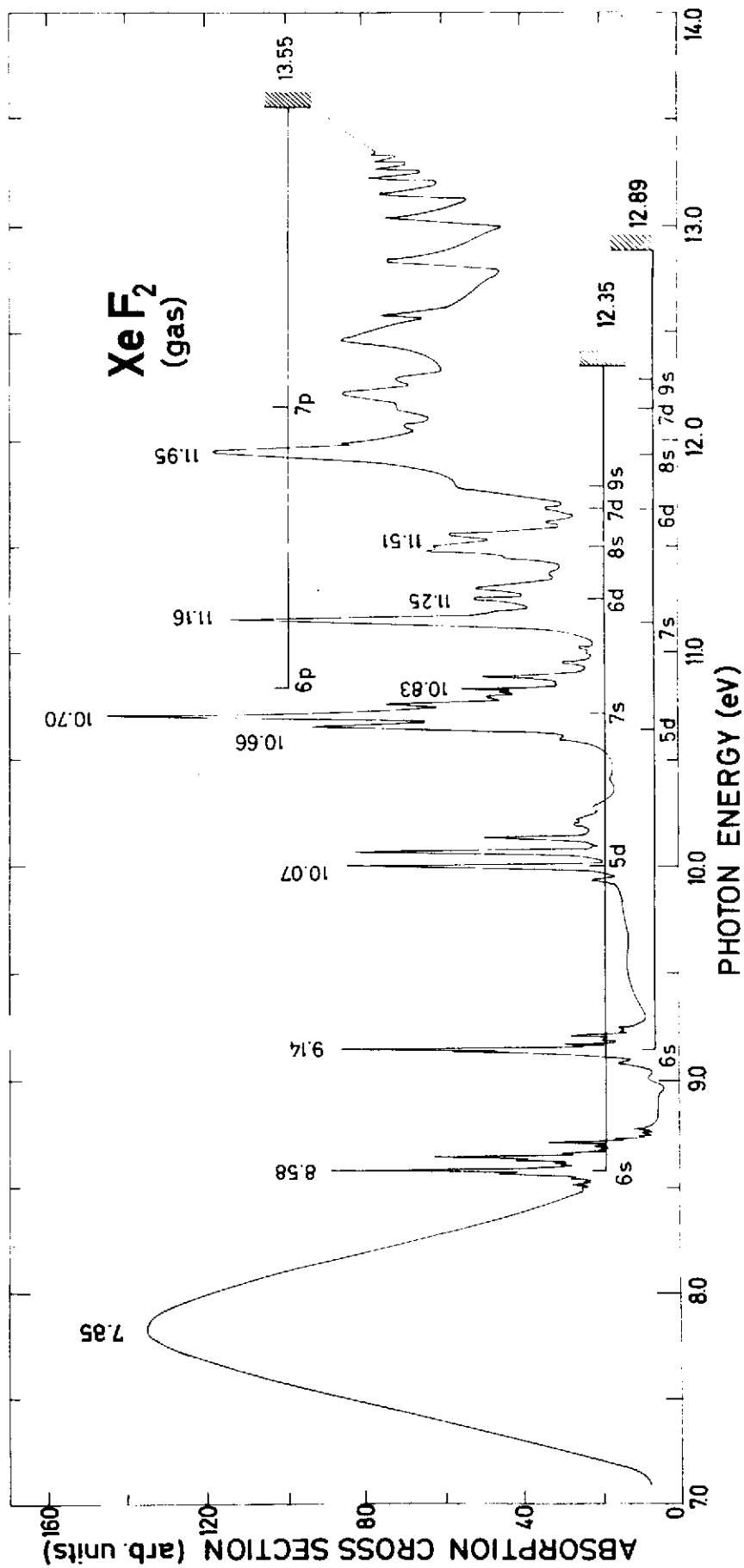6p 7p 8p a_{1g} e_g, 2 x t$_{2u}$ t_{1u}
                                  t_{1g}, t_{2g}

Fig. 3

Fig. 4

Fig. 5

Fig. 6

XeF₂ (gas)

ABSORPTION CROSS SECTION (arb. units)

PHOTON ENERGY (eV)

Fig. 7