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2 HAMBURG 52 · NOTKESTIEG 1

The Optical Spectra of Gaseous and Solid SF_6 in the Extreme Ultraviolet and Soft X-Ray Region

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The reflectivity of solid SF_6 has been measured in the energy range of 10 to 30 eV, the absorption of solid SF_6 between 170 and 300 eV. For comparative purposes the absorption spectrum of the free molecule has also been obtained in the same energy range. The experimental results strongly support the concept of an effective potential barrier around the central S atom, as recently developed by Dehmer.

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I. INTRODUCTION

From many points of view SF_6 is a very interesting molecular gas and its electronic structure as well as the different electronic transitions within the molecule have been investigated by several methods. Photoelectron[1,2] photoionization[3,4] and inelastic electron scattering measurements have been performed. In the latter case[5] the photoabsorption curve has been deduced from the loss function. Several authors have carried out direct optical measurements. Codling[6] observed a vibrational progression and weak Rydberg series and measured the absolute photoabsorption cross section for 3 energies above the first ionization limit in the energy range 20.6 to 26.11 eV where valence shell excitations occur. Similar results have been obtained by Sasanuma et al.[7]. The S K(1s) spectrum (2450 eV to 2900 eV) has been studied by LaVilla and Deslattes[8], the F K(1s) spectrum (680 eV to 760 eV) by Zimkina and Vinogradov[9]. Zimkina and Fomichev[10] observed strong absorption lines in the $L_{II,III}$(2p) spectrum of S (170 eV to 300 eV). No Rydberg structure has been observed in these inner shell transition spectra; only recently did Nakamura et al.[11] detect weak Rydberg series between the strong absorption lines of the S $L_{II,III}$(2p) spectrum.

Molecular orbital calculations have been performed by Gianturco et al.[12] and by Connolly and Johnson[13].

To obtain additional information on the nature of the electronic structure of SF_6 we have performed optical measurements on solid SF_6. Comparison of the optical spectra of materials in the gaseous and solid state in the same energy region allows us to obtain information on the locality or non-locality of transitions.

II. EXPERIMENTAL SETUP

The experiments were performed using the synchrotron radiation of the 7.5 GeV electron synchrotron DESY[14,15].

In the long wavelength region up to 30 eV (in the following referred to as the VUV spectrum) the measurement of solid SF_6 was performed by reflection since the substrate problem for absorption measurements is severe in this energy range. The reflectivity measurements were made in an ultra-high vacuum reflectometer[16] attached to a normal incidence monochromator in a modified Wadsworth mount[17]. The wavelength resolution was 2 Å over the whole energy range. The experimental setup and procedures were the same as those used for the study of solid rare gases[18]. The gas absorption measurements were made in another instrument of similar design[19] achieving a wavelength resolution of 1 Å.

In the short wavelength region between 170 and 300 eV (in the following referred to as the XUV spectrum) the absorption measurements were made with a grazing incidence spectrometer yielding a wavelength resolution of 0.1 Å. The experimental arrangement and procedure were the same as those used for similar measurements on atomic and solid rare gases[20].

III. RESULTS AND DISCUSSION

Figures 1 and 2 show the experimental results. In Fig. 1 we see the results for the VUV region. The gas absorption data are compared with data from Simpson et al.[5] obtained by conversion of their electron energy loss data, and also with 3 experimental data points obtained by Codling[6].

The long wavelengths VUV reflection spectrum of solid SF_6 shows three main peaks at 16.7, 19.6 and 23.0 eV. A reduction of the reflection to a ε_2 curve was not performed, because the usual rule for reflectivity values up to 20 % shows, that the main character of the spectra remains unchanged although the peaks may be slightly changed in the ε_2 curve as regards energy position and oscillator strength. Although the absolute reflectivity (never exceeding 10 %) changed with different experimental conditions (e.g. evaporation speed) the general shape of the spectrum remained unchanged.

We would like to emphasize that the two VUV spectra of gaseous and solid SF_6 are remarkably different; in the region between 10 and 16 eV where pronounced fine structure in the gas can be seen, we only find a rather smooth increase of the reflectivity in the solid. In the range between 16 eV and 30 eV the spectra of the gas and the solid seem to have some similarity.

The situation is completely different in the XUV region (Fig. 2). Here the absorption spectra of gaseous and solid SF_6 are equal within the experimental errors. Both spectra are in good accordance with the data from Zimkina and Fomichev[10]; only the energy positions of the absorption maxima are slightly different for the two measurements.

Our experimental results are in excellent agreement with recent theoretical considerations made by Dehmer[21]. The valence states are formed from atomic S 3s and 3p and F 2p states. The four outermost molecular orbitals occupied in the ground state are entirely formed from atomic F states. As the F^- ions are in the outer part of the molecule they are affected by the next neighbours in the solid, even though the binding is essentially the weak van der Waals binding force. Thus it can easily be explained that the molecular and solid state VUV spectra are quite different as regards excitations from these outermost orbitals.

This is no longer true for the other occupied valence orbitals formed from atomic S and F states. The bands observed around 23 eV in both the vapour and the solid state may have the same origin. One may tentatively assign them to transitions from the molecular orbitals formed both from the S 3s, 3p and F 2p atomic states ($4t_{1u}^{(6)}$, $5a_{1g}^{(2)}$, see e.g. the correlation diagram in Ref. 21). As regards the excitations from the S $L_{II,III}$(2p) orbitals (Fig. 2) all the transitions take place between rather localized states within the effective potential barrier formed by the surrounding F^- ions. They are, therefore, hardly affected by the chemical surroundings in the solid. The interpretation of the strong absorption lines in the molecule given by Dehmer[21] may be transferred to the solid state spectra in a straightforward manner. The doublet structure at 173.4 eV has been assigned to the transition $2t_{1u} \rightarrow 6a_{1g}$, the doublet at about 184 eV to $1t_{1u} \rightarrow 2t_{2g}$ and the peak at 196.5 eV to $2t_{1u} \rightarrow 4e_g$. All final states are inner-well states i.e. resonances within the potential well around the central S atom nucleus. Thus the identity of the gaseous and solid state spectra is easily explained.

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References

1. D.C. Frost, C.A. McDowell, J.S. Sandhu, and D.A. Vroom J.Chem.Phys. 46, 2008 (1967)
2. K. Siegbahn, C. Nordling, G. Johansson, J. Hedman, P.F. Hedén, K. Hamrin, U. Gelius, T. Bergmack, L.O. Werme, R. Manne, and Y. Baer, *ESCA Applied to Free Molecules* (North Holland Publishing Company, Amsterdam - London 1969) p. 94
3. V.H. Dibeler and J.A. Walker, J.Chem.Phys. 44, 4405 (1966)
4. R.N. Compton, R.H. Huebner, P.W. Reinhardt, and L.G. Christophorou, J.Chem.Phys. 48, 901 (1968)
5. J.A. Simpson, C.E. Kuyatt, and S.R. Mielczarek, J.Chem.Phys. 44, 4403 (1966)
6. K. Codling, J.Chem.Phys. 44, 4401 (1966)
7. M. Sasanuma, E. Ishiguro, Y. Morioka, and M. Nakamura, paper 1pA2-3 given at the III. International Conference on Vacuum Ultraviolet Radiation Physics, Tokyo, Japan (1971), unpublished
8. R.E. LaVilla and R.D. Deslattes, J.Chem.Phys. 44, 4399 (1966)
9. T.M. Zimkina and A.C. Vinogradov, J.Phys. (France) to be published
10. T.M. Zimkina and V.A. Fomichev, Dokl. Akad. Nauk. SSSR 169, 1304 (1966) (Engl. Transl.: Sov. Phys. - Dokl. 11, 726 (1966))
11. M. Nakamura, Y. Morioka, T. Hayaishi, E. Ishiguro, and M. Sasanuma, paper 1pA1-6 given at the III. International Conference on Vacuum Ultraviolet Radiation Physics, Tokyo, Japan (1971), unpublished
12. F.A. Gianturco, C. Guidotti, U. Lamanna, and R. Moccia, Chem.Phys. Letters 10, 269 (1971)
13. J.W.D. Connolly and K.H. Johnson, Chem.Phys. Letters 10, 616 (1971)
14. R. Haensel and C. Kunz, Z. Angew. Phys. 23, 276 (1967)
15. R.P. Godwin, in *Springer Tracts in Modern Physics*, ed. G. Höbler (Springer Verlag, Berlin 1969) Vol. 51, p. 1

16. B. Feuerbacher, R.P. Godwin, and M. Skibowski, Rev.Sci.Instr. 40, 305 (1969)

17. M. Skibowski and W. Steinmann, J.Opt.Soc.Am. 57, 112 (1967)

18. R. Haensel, G. Keitel, E.E. Koch, M. Skibowski, and P. Schreiber, Opt. Comm. 2, 59 (1970) and references therein

19. E.E. Koch and M. Skibowski, Chem.Phys.Letters 9, 429 (1971)

20. R. Haensel, G. Keitel, P. Schreiber and C. Kunz, Phys.Rev. 188, 1375 (1969)

21. J.L. Dehmer, J.Chem.Phys. (to be published)

Figure Captions

Fig. 1 Absorption of gaseous SF_6 and reflectance of solid SF_6 in the VUV region. Data obtained by Simpson et al.[5] and Codling[6] are given for comparison.

Fig. 2 Absorption spectra of gaseous and solid SF_6 in the XUV region. The absorption spectrum of gaseous SF_6 obtained by Zimkina and Fomichev[10] is given for comparison.

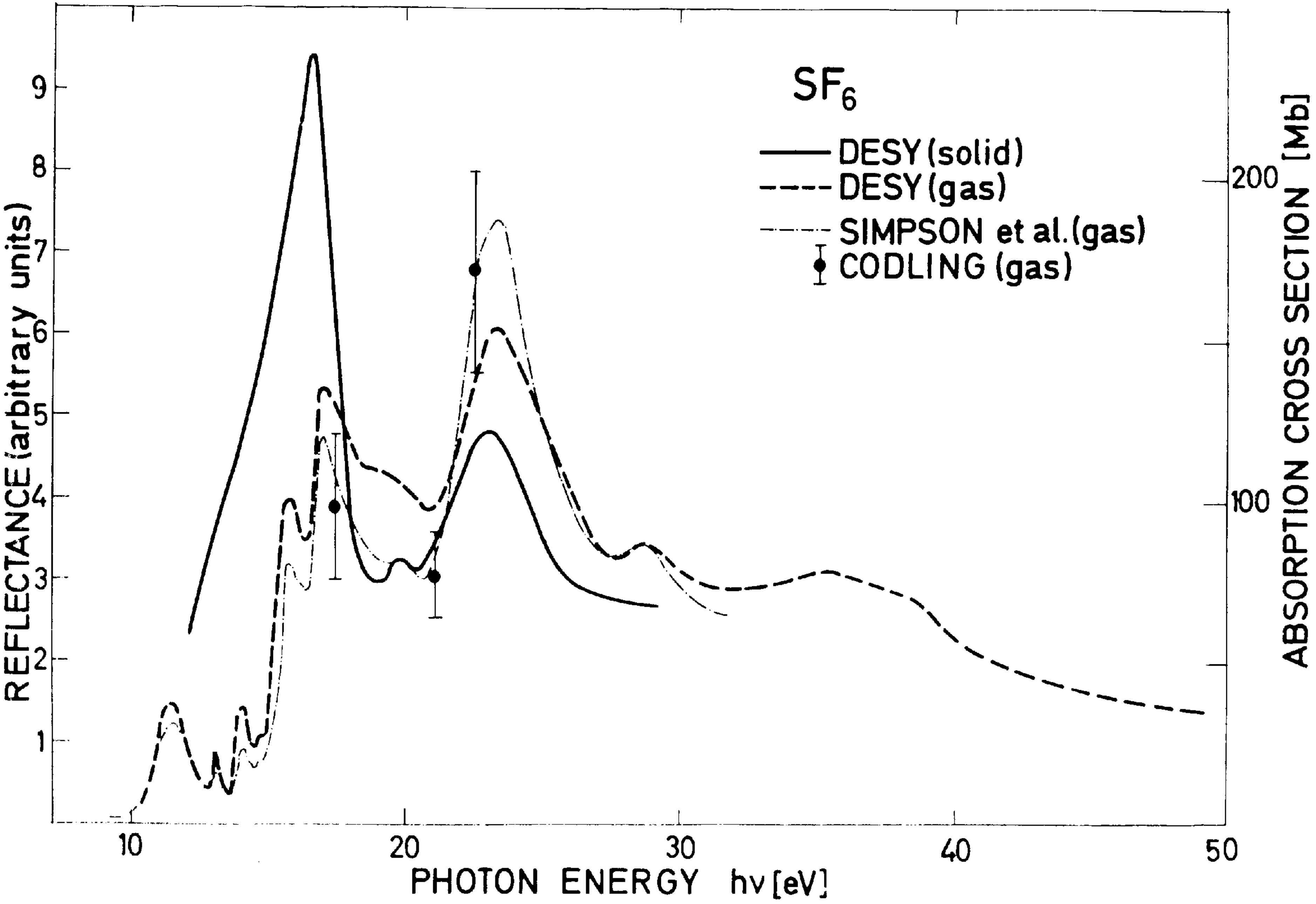
SF$_6$
DESY (solid)
DESY (gas)
SIMPSON et al. (gas)
CODLING (gas)
REFLECTANCE (arbitrary units)
1
2
3
4
5
6
7
8
9
ABSORPTION CROSS SECTION [Mb]
100
200
10
20
30
40
50
PHOTON ENERGY hν [eV]

Fig. 1

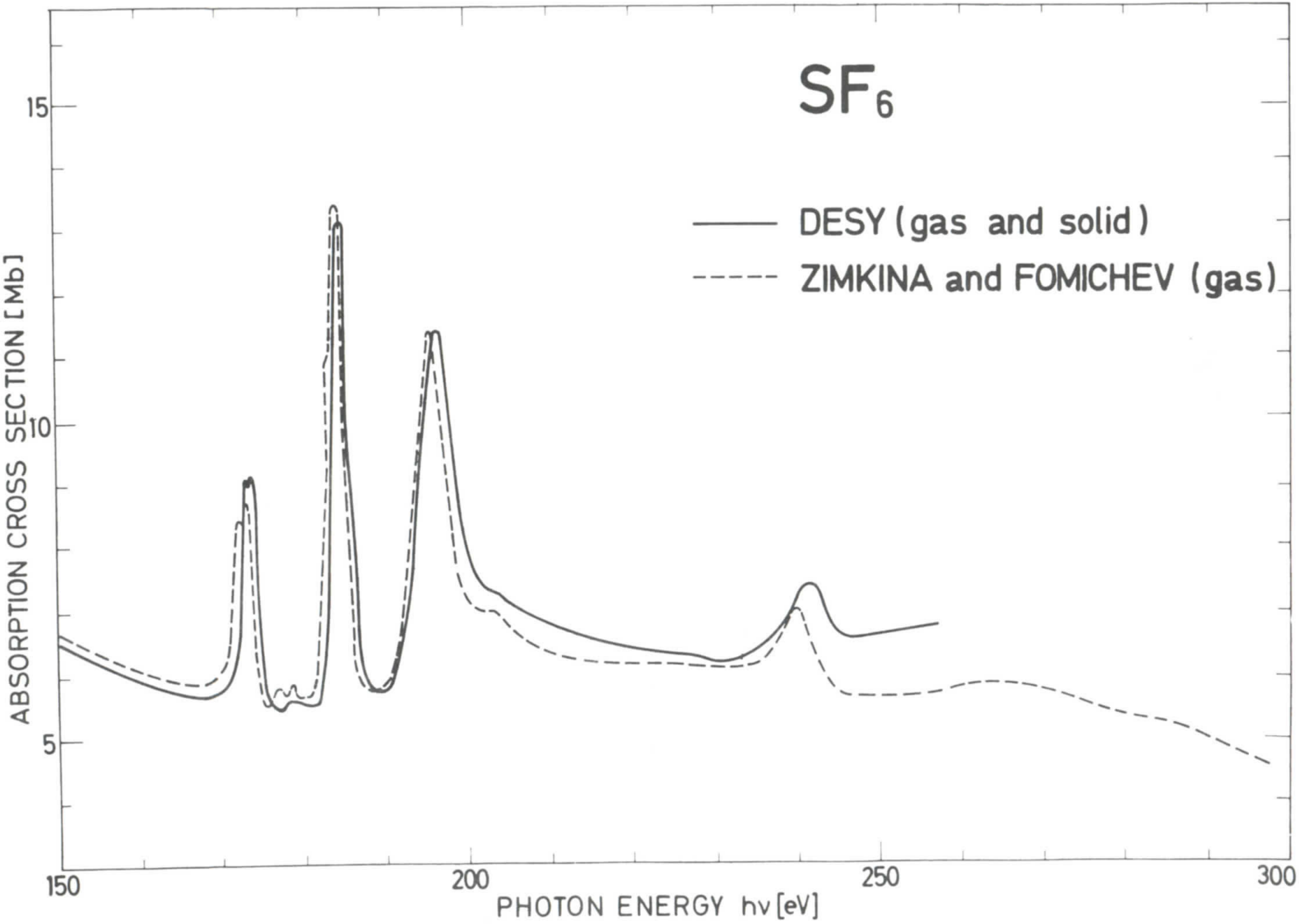
SF6
DESY (gas and solid)
ZIMKINA and FOMICHEV (gas)
ABSORPTION CROSS SECTION [Mb]
15
10
5
150
200
250
300
PHOTON ENERGY hν [eV]

Fig. 2