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PHOTOELECTRON AND PENNING IONIZATION ELECTRON SPECTROSCOPIC INVESTIGATION OF TRIMETHYLPHENYLSILANE

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Summary

Penning ionization electron spectroscopy and CNDO/S calculations have been succesfully applied to the analysis of the UV photoelectron spectrum of trimethylphenylsilane.

The Ultraviolet Photoelectron Spectrum (UPS) of trimethylphenylsilane is well-known and appeared even in the pioneering work of Turner [1]. However, the assignment of the observed bands has been limited to the first two peaks [2,3].

Very recently Penning Ionization Electron Spectroscopy (PIES) has been successfully applied to the analysis of the UPS of some unsaturated molecules [4–6]. The most important difference between the photoelectron and Penning electron spectra is that the π bands in the Penning spectra are enhanced relative to the σ bands. We have now made a detailed assignment of the bands in the UPS of trimethylphenylsilane on the basis of CNDO/S calculations [7] and use of the Penning spectra.

Experimental

The electron spectra were obtained at an ejection angle of 90° with respect to the metastable or the photon beams by means of a hemispherical analyzer. The sample vapor was introduced into the collision chamber through a nozzle at ca. 25°C. Metastable neon atoms, Ne* ($^3P_2$, 16.62 eV) were produced by impact of 60 eV electrons; at this energy the contributions of Ne* ($^3P_0$, 16.72 eV) atoms and photons are negligible [4]. For the measurement of the UPS, pure helium and neon gas discharges were used to produce the He(I) (21.21 eV) and Ne(I) (16.85 and 16.67 eV) radiations. The low energy component of the Ne(I) lines made little contribution to the spectra.

Results and discussion

In Fig. 1 the He(I) photoelectron spectrum of trimethylphenylsilane is compared with those of benzene and tetramethylsilane. The first two peaks of the spectrum are derived from the e_{1g} (π) orbitals of benzene. The splitting of the orbitals is small, being less than 0.3 eV. The next broad band between 10 and 11 eV, with medium intensity, is derived from tetramethylsilane. The original band in tetramethylsilane having t_1 symmetry is broadened by the Jahn-Teller effect [8]. In trimethylphenylsilane the degeneracy of the orbitals is removed, and the band due to three separated orbitals is expected in this region. In the next portion of the spectrum the e_{2g} (σ) and a_{2u} (π) bands in benzene appear between 11.5 and 12.1 eV. The band at 12.8–13.5 eV is due to $SiMe_4$ and that between 13.8 and 14.5 eV can be related to both parent compounds. The origin of the band at 15.65 eV is uncertain. The peaks at 16.6 may be derived from the benzene a_{1g} orbital (in benzene: 16.84 eV). By comparison with the spectra of the two parent compounds in this region, it can be assumed that the peak at 17.0 eV also belongs to the a_{1g} band with another vibrational transition. The energy difference between the two peaks is 0.4 eV ~ 3000 cm^{-1}. Taking into account the ring stretching (breathing) mode frequency of benzene (992 cm^{-1}) it seems that a 0–3 transition is the most likely in the ionized state. This, by the Franck-Condon principle, may refer to a strong streching of the molecule in the ionized state.

The Ne(I) UPS and Ne* PIES of $PhSiMe_3$ are shown in Fig. 2. It must be

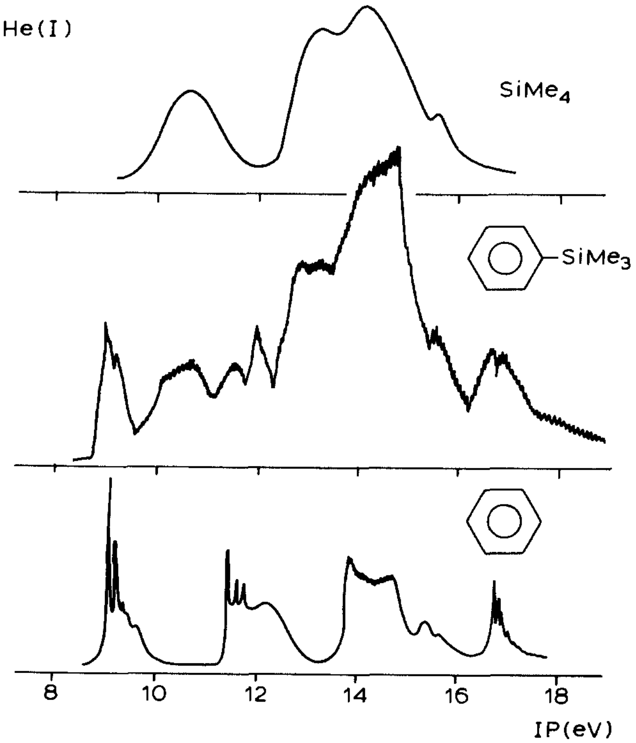

Fig. 1. He(I) photoelectron spectrum of benzene, trimethylphenylsilane and tetramethylsilane.

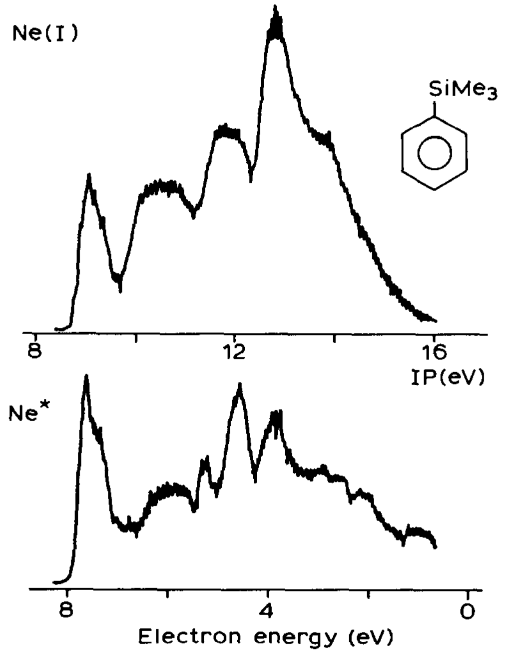

Fig. 2. Ne(I) UPS and Ne* PIES of trimethylphenylsilane.

emphasized that the IP scale in Fig. 2 refers only to the UPS. In the case of PIES the abscissa refers to the energy of ejected electrons. (Approximately IP = 16.62 eV $- E_{\text{electron}}$).

In Fig. 2. we find that the first band due to the benzene e_{1g} (π) orbital is enhanced in the PIES, conforming with the trend observed in the references [4–6].

TABLE 1

OBSERVED AND CALCULATED IONIZATION POTENTIALS (eV)

Trimethylphenylsilane			Assignment [a]	Benzene	
observed	calc.(CNDO/S)			observed	calc.(CNDO/S)
	without *d* orbitals	with *d* orbitals			
9.05	8.80	8.91	e_{1g} (π_3)	9.25	9.03
9.30	8.98	9.01	e_{1g} (π_2)	9.25	9.03
10.10	10.16	10.19	Si–C_{Ar}		
10.70	10.89	10.96	Si–C_{Me}		
	11.11	11.14	Si–C_{Me}		
11.60	11.95	11.99	e_{2g} (σ)	11.53	11.98
12.05	12.33	12.36	a_{2u} (π_1)	12.38	12.35
12.8	12.84	12.92	e_{2g} (σ)	11.53	11.98

[a] The bands due to the benzene ring are correlated with benzene orbitals.

Further, the band at 11.5–12.1 eV in the UPS is split into two separate peaks in the PIES, of which the first is weak and the second remarkably intense. Therefore, the latter peak can be assigned to the π_1 orbital.

In Table 1 the ionization potentials (IP) of $PhSiMe_3$ calculated by the CNDO/S method are compared with those observed ones. Table 1 also contains the calculated and observed IP's of benzene. (In our experience [7] the calculated and observed ionization potentials are linearly related as follows: $IP_i = -0.74\ \varepsilon_i + 1.70$ eV. The calculated values in Table 1 have been modified by use of this formula.) It will be seen from Table 1 that there is no substantial difference between the calculated values obtained with and without *d* orbitals, although the orbital energies are somewhat lower in the calculation including *d* orbitals. The calculations support the conclusions stated above. The band between 10 and 11 eV comprises three orbitals, mainly distributed over the $Si–C_{Ar}$ and $Si–C_{Me}$ bonds. The degenerate e_{2g} (σ) MO's of benzene are split and the position of one of them (a'') is almost unchanged because the nodal plane of this MO is in the direction of the $Si–C_{Ar}$ bond. The other orbital (a') is stabilized strongly. Thus the π_1 orbital is situated between the two orbitals due to the e_{2g} (σ).

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