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Valence and C 1s core level photoelectron spectra of camphor

Emma E. Rennie[a,b], Ivan Powis[c,*], Uwe Hergenhahn[a,b], Oliver Kugeler[a,b],
Gustavo Garcia[c], Toralf Lischke[a], Simon Marburger[a]

[a]*Fritz-Haber Institut der Max Planck Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany*
[b]*Max-Planck-Institute for Plasma Physics, Boltzmannstrasse 2, D-85748 Garching, Germany*
[c]*School of Chemistry, University of Nottingham, Nottingham NG7 2RD, UK*

Abstract

The valence photoelectron spectrum of camphor has been recorded with 95 eV synchrotron radiation, with better definition than previous He I spectra. The spectrum is interpreted by comparison with these He I results and with the aid of an outer-valence Green's Function calculation of the orbital ionization energies. These calculations closely reproduce the observed vertical ionization energies in the outer valence region. A core level spectrum of the C 1s region ($h\nu=357.9$ eV) is also presented and reveals a marked shift of the carbonyl carbon relative to all others in the molecule.
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1. Introduction

The ultraviolet photoelectron spectra of camphor (Fig. 1) has been reported by a number of authors [1–3], in each case as part of wider ranging comparative study of structural influences in related series of bicyclic, carbonyl containing compounds. Limited assignments and interpretations of the valence bands of camphor have been made on the basis of such comparisons. The low vapour pressure of camphor necessitates using a heated source for such studies and, perhaps as a consequence of ensuing experimental difficulties, these existing He I ($h\nu= 21.2$ eV) spectra are of modest resolution. Moreover

there are some significant, unexplained differences in the band intensities in spectra recorded under very similar nominal conditions [1,3].

In this paper we present the camphor photoelectron spectrum measured with higher energy (95 eV) synchrotron radiation. The higher photon flux of the synchrotron radiation allows an improvement in the signal-to-noise ratio obtained, while differences in relative band intensity observed with these higher photon energies may provide further insight into the outer valence region. Additionally, the extended energy range permits the first examination of the inner valence region of this molecule. Assignment and interpretation are here assisted by a theoretical calculation of the vertical ionization energies.

Complementing these ultraviolet valence region studies on camphor we also include the first C 1s core level photoelectron spectrum of the camphor

*Corresponding author. Tel.: +44-115-951-3467; fax: +44-115-951-3562.
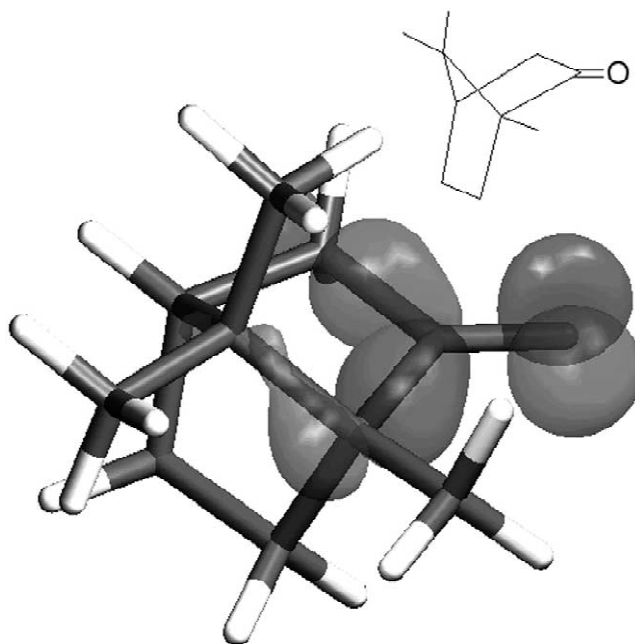
E-mail address: ivan.powis@nottingham.ac.uk (I. Powis).

Fig. 1. R-($+$)-camphor and the calculated RHF cc-pVDZ HOMO, nominally the carbonyl n_O orbital.

molecule. This reveals a marked shift of the position of the carbonyl carbon peak relative to all others, in large measure in response to the valence electron distribution in the molecule.

2. Experimental details and data analysis

The spectra were recorded on the UE56/2-PGM [4] undulator beamline at the BESSY II synchrotron radiation source in Berlin with a Scienta SES-200 hemispherical electron spectrometer [5] mounted in a large spherical chamber. The analyser was mounted outside of the dipole plane, under a forward scatter-ing angle of 54.7° with respect to the beam direction. All of the spectra in this work were measured with circularly polarised light. Under these conditions the electron acceptance of the analyser is set at the 'magic' angle so that measurements should be insensitive to the photoelectron asymmetry parame-ter, β.

Commercial samples of camphor (Aldrich>95% enantiomeric purity), which is a solid at room temperature, were admitted into the chamber via a heated gas line at ~80 °C. The vapour then entered a

heated gas cell inside the main vacuum chamber where photoionization occurred. The gas cell in-corporated apertures for the synchrotron radiation and photoelectrons, as well as a photoelectron dump to prevent backscattered electrons from entering the analyser.

R-($+$)-camphor valence spectra were recorded with an incident photon energy of 95 eV using a 400 l/mm grating. The wide range overview spectra were obtained with a beamline exit slit setting of ~180 μm, an electron analyser slit width of 1.0 mm and a pass energy of 75 eV, corresponding to an overall estimated resolution of 500 meV. Higher resolution spectra were obtained with a beamline exit slit setting of ~100 μm, an electron analyser slit width of 0.5 mm and a pass energy of 75 eV, corresponding to overall estimated resolution of 300 meV. The incident photon energy and spectrometer kinetic energies were calibrated using binding energies for the xenon 5 s main and satellite photoelectron lines [6], which were measured with an incident photon energy of 111 eV. Typically two or three identical spectra were recorded and saved separately, then summed allowing for small shifts in kinetic energy. The pressure in the main chamber was ~8×10^{-6}

mbar. Two of the high resolution camphor (+) spectra were measured with opposing light helicities and were found to be identical.

The S-(−)-camphor C 1s core level spectra were measured with incident photon energies of 357.9 eV, also with the 400 l/mm grating. The incident photon energy was calibrated using the argon 2p photoelectron lines. The spectra were obtained with a beamline exit slit setting of ~60 μm, an electron analyser slit width of 0.2 mm and a pass energy of 40 eV, corresponding to an overall estimated resolution of 90 meV. The pressure in the main chamber was ~1×10^{-5} mbar. Several identical spectra were recorded and saved separately, then summed allowing for small shifts in kinetic energy. Again, checks were made recording spectra with opposing circular polarisations and/or the R-(+) enantiomer. At this photon energy only negligible differences (<1%) were noted in relative intensities.

3. Computational details

Calculations were performed using the Gaussian 98 and GAMESS (UK) packages. Optimised geometrical parameters for the camphor molecule were obtained from a density functional theory (DFT) calculation performed using a B3LYP functional [7,8] and 6-31G** basis set. All subsequent calculations were performed at this optimised geometry. Theoretical estimates of the vertical ionization energies, I_{vert}, were calculated using an outer-valence Green's Function (OVGF) method [9,10] using cc-pVDZ basis. These results are shown in Table 1.

4. Results and discussion

A wide range $h\upsilon$=95 eV overview spectrum, spanning ionization energies up to 41 eV is presented in Fig. 2. Representations of earlier He I spectra [1,3] are included for comparison. The extended energy range of the current work allows the observation of a number of distinct additional bands in 20–24 eV region of the spectrum, with two further broad, diffuse structures centred around 26.5 and 32.5 eV. There are also differences in relative band intensity below 20 eV, the most marked of which is

Table 1

Experimental and calculated vertical ionization energies for Camphor

Calculated values		Experimental I_{vert} (eV)		
I_{vert} (eV)	Pole strength	This work (±0.05 eV)	Ref. [3]	Ref. [1]
8.74	0.90	8.70	8.7	8.95
10.27	0.91	10.25	10.3	10.4
10.85	0.91	10.80		
11.04	0.91		11.0	
11.43	0.91	11.30		
11.93	0.90			
12.02	0.91	12.05	12.1	
12.41	0.90			
13.14	0.91	13.10	13.1	
13.17	0.91			
13.45	0.91	13.55		
13.73	0.91			
13.77	0.90	13.85	13.9	
13.98	0.91			
14.26	0.91			
14.36	0.89			
15.12	0.90	15.10		
15.64	0.89	15.55		
16.10	0.89	15.90	16.1	
16.16	0.90			
16.65	0.88	16.40	16.4	
17.82	0.88	17.45	17.4	
19.31	0.88	18.65	18.7	
20.96	0.87	20.40		
21.83	0.86	21.50		
22.50	0.86			
23.70	0.83	23.65		

The theoretical results are obtained from OVGF calculations using a cc-pVDZ basis at the B3LYP/6-31G** optimised molecular geometry

the greatly enhanced relative intensity of the outermost band at 8.7 eV in the $h\upsilon$=95 eV spectrum. Such an increase is fully consistent with the assignment of this lowest energy band to the carbonyl oxygen lone pair orbital (n_O), it being empirically established that orbitals with a large atomic O 2p character are expected to gain in intensity relative to skeletal C–C bonds with increasing photon energy [11].

From comparative studies of the width of nominally n_O lone pair orbitals in related molecules an interaction with other nearby orbitals has been deduced for camphor [3]. This expectation is borne out by the detailed molecular orbital calculations in the present study which show a clear mixing of the O
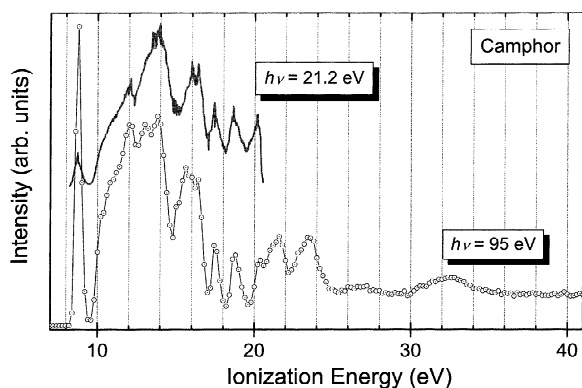
Fig. 2. The valence photoelectron spectrum of camphor recorded with a 95 eV photon energy. Also shown is a redrawn He I spectrum [3].
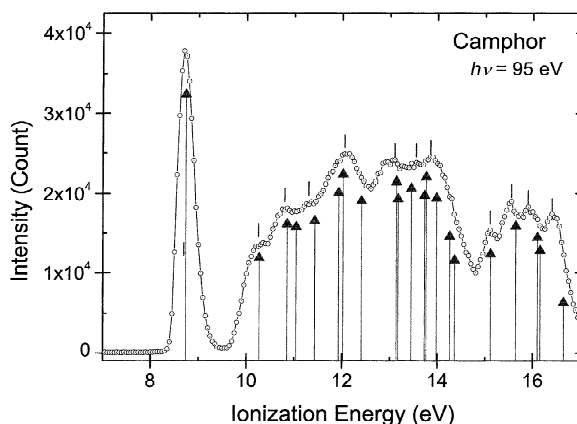

Fig. 3. Expanded outer valence region of the $h\nu=95$ eV photoelectron spectrum. Experimental peak positions are marked with a tick, while the calculated OVGF cc-pVDZ I_{vert} values are indicated by arrows drawn from the axis. The length of the arrows is chosen to guide the eye.

lone pair with C–C σ orbitals adjacent to the carbonyl group in the highest occupied molecular orbital (Fig. 1). As a corollary some atomic O 2p character is found to be mixed in to the next two C–C σ orbitals so that these might also be expected to show some increase in relative intensity with increased photon energy in the spectrum. Comparing the $h\nu=95$ eV and $h\nu=21.2$ eV spectra [3] in Fig. 2 (as well as the independent He I spectrum of Pollmann et al. [2] not explicitly shown here) one sees that the relative intensities of those orbitals with ionization energies <13 eV are indeed greater at the higher photon energy. While these two comparisons provide experimental support for the mixing of n_O character into near lying σ orbitals, it should be noted that the third published He I spectrum [1] displays a very different intensity distribution across the range 10–20 eV, perhaps as a consequence of uncorrected analyser transmission or angular discrimination effects.

A higher resolution scan of the outer valence region is shown in Fig. 3. The indicated experimental peak positions are listed in Table 1 along with the calculated I_{vert} values. These results reveal more structure in the spectrum than hitherto observed. There is excellent agreement between the experimental and calculated HOMO (n_O) I_{vert} values and an impressive correspondence across the range. The most notable shortcoming is that the calculated peaks at $I_{vert}=12.41$, 13.98, 14.26, and 14.36 eV fail to correspond to any pronounced features in the ex-

perimental spectrum. This indicates that these ionizations are, at the least, rather weaker than the others and so are substantially hidden under the high energy tail of the peaks seen at either 12.05 or 13.85 eV. The calculated pole strengths of these transitions do not differ significantly from any of the others, suggesting that while they are not inherently weaker the associated Franck–Condon factors may be poor.

Three of the four orbitals corresponding to these problematic weak ionizations are found to have localised bonding character at the carbonyl group: C=O π bonding (12.41 eV); C–O σ bonding (14.26 eV); and a mixed σ/π bonding character (14.36 eV)—the latter interaction reflecting the lowered symmetry of the molecule as a whole. It therefore seems quite plausible that with such localised bonding character big geometric changes at the carbonyl group might result from ionization, with the consequence of poor Franck–Condon factors as inferred above. In contrast, ionization of delocalised electrons bonding the rigid C skeleton, or of non-bonding electrons, should lead to less geometric change, with more favourable vibrational overlap.

The photoelectron spectrum of the inner valence region up to 26 eV is shown in Fig. 4. The correspondence between calculated I_{vert} values and experimental peak positions is apparently less good in this region. The OVGF calculation uses a purely
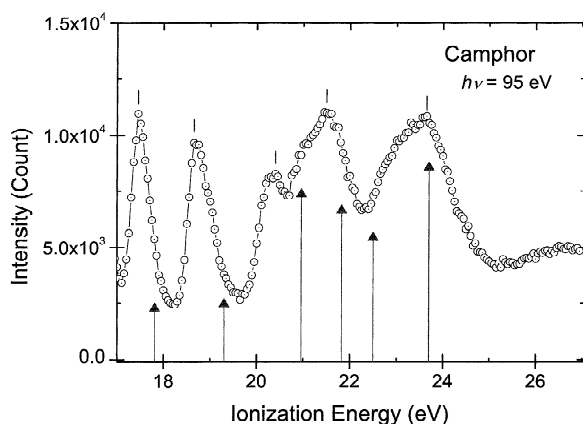
Fig. 4. Inner valence region to I.E. 27 eV. Details as for Fig. 3.

Fig. 5. C 1s core ionization spectrum.

one-particle model for the photoionization [9,10]. It is well recognised that as electron correlation becomes increasingly more important in deeper lying orbitals, an independent particle photoionization model will break down, so that this poorer agreement is not unexpected. In fact it can be seen that there is a trend starting around 16 eV for the calculation to increasingly overestimate the experimental ionization energies. But by applying an empirical reduction in the calculated I_{vert} values it is still possible to identify a one-to-one correspondence between theoretical and experimental peaks in this region (with the supposition that a small shoulder seen in the experimental spectrum at I.E. = 21 eV is actually the additional, but barely resolved, band associated with the calculated 21.83 eV ionization). Only for the diffuse bands above 26 eV does the independent electron model fail more comprehensively.

In Fig. 5 we present a photoelectron spectrum taken in the C 1s core ionization region. This can be assigned with the aid of calculated eigenvalues for the C 1s orbitals. The results of various model calculations are given in Table 2. The carbonyl C 1s orbital is always lowest in energy, with the remaining C 1s levels being presented in ascending order. There is a clear separation in energy of the carbonyl carbon atom from the others, but not unexpectedly the Koopmans's theorem estimates of the ionization energies are not in exact agreement with experiment.

In practice, such estimates from the Hartree–Fock (HF) eigenvalues could be expected to overestimate the binding energy, since relaxation in the core hole
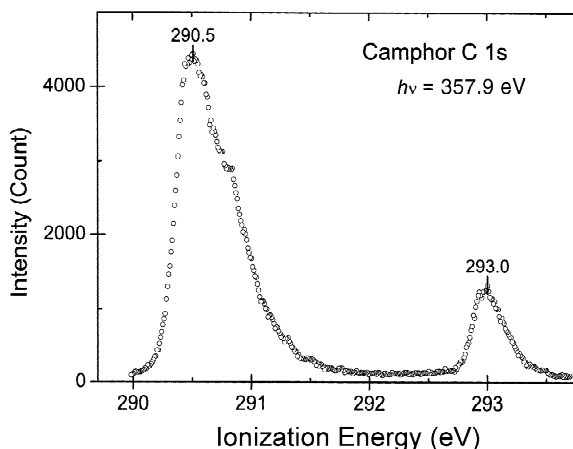
state is ignored. And Koopman's theorem does not strictly apply to the DFT Kohn–Sham orbitals calculated with present-day functionals like B3LYP. However, studies suggest that relative ionization energies may still be meaningfully estimated from DFT results [12] and that the eigenvalues may be related to the Koopman's theorem limit by a simple linear correlation [13]. More particularly, these studies find that Kohn–Sham orbitals are generally shifted to higher (less negative) energy than their HF counterparts and are consequently more likely to lead to an underestimate the binding energy. Overall, the HF and DFT eigenvalues should generate estimates which bracket the experimental ionization energy and both should reliably indicate the expected shifts.

The HF and DFT Koopman's theorem estimates from the eigenvalues listed in Table 2 do indeed bracket the experimental values and lead to an unambiguous assignment with the smaller peak (experimental I_{vert} = 293.0 ± 0.1 eV) being clearly identified as the carbonyl C 1s ionization. All other C 1s levels are largely overlapped under the main peak (experimental I_{vert} = 290.5 ± 0.1 eV), though some structure can be discerned to high energy on the experimental peak as might be expected from the calculated spread of shifts about the mean for these skeletal C peaks seen in Table 2. The experimental I_{vert} splitting (2.5 eV) is also in good accord with the mean splitting seen in the eigenvalues in Table 2.

The carbonyl C 1s peak has been closely examined for any vibrational structure, but is essential-

Table 2
C 1s eigenvalues from indicated RHF and DFT calculations

	cc-pVDZ/RHF	ΔE	cc-pVDZ/b3lyp	ΔE	6-31G**/b3lyp	ΔE
C=O Eigenvalue	−308.150		−279.312		−279.290	
Others . . .	−306.089	2.06	−277.657	1.65	−277.640	1.65
	−305.912	2.24	−277.448	1.86	−277.437	1.85
	−305.862	2.29	−277.409	1.90	−277.383	1.91
	−305.785	2.36	−277.331	1.98	−277.286	2.00
	−305.737	2.41	−277.238	2.07	−277.195	2.10
	−305.684	2.47	−277.235	2.08	−277.190	2.10
	−305.538	2.61	−277.071	2.24	−276.982	2.31
	−305.536	2.61	−277.062	2.25	−276.979	2.31
	−305.381	2.77	−276.927	2.38	−276.840	2.45
Mean splitting		2.42		2.05		2.08

Splittings from the lowest (CO) eigenvalue are shown in each case. All values in eV.

ly structureless, despite it having a full-width half maximum (FWHM, ~300 meV) which is greater than the experimental resolution (~90 meV) and greater than typical C 1s lifetimes which correspond to a width of 70–100 meV.

5. Summary

The use of synchrotron radiation has permitted us to obtain photoelectron spectra of camphor extending to more than 40 eV kinetic energy in the valence region, and spanning the C 1s levels in the core region. Despite the low symmetry of the molecule, which precludes a facile characterisation and labelling of the valence orbitals, it is possible to gain some insight from ab initio calculations which provide a convincing model for the spectrum. Particulary, it is seen that those orbitals localised on the carbonyl group are either enhanced at higher photon energies if they have n_O lone pair character, or are prone to being suppressed, seemingly as a consequence of poor Franck–Condon factors, when they possess C–O bonding character.

The spectra were recorded at the magic angle with circularly polarized radiation, in order to suppress the effects of electron angular discrimination. Additionally, since camphor is a chiral molecule, checks were made to establish that the spectra presented here were not sensitive to the selected helicity of the radiation. However, under other circumstances we have found preliminary evidence for such chiral

sensitivity, and these results will be presented in future papers.

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