

# The electronic states of 2-furanmethanol (furfuryl alcohol) studied by photon absorption and electron impact spectroscopies

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The photoelectron spectrum of 2-furanmethanol (furfuryl alcohol) has been measured for ionization energies between 8 and 11.2 eV and the first three ionization bands assigned to  $\pi_3$ ,  $\pi_2$ , and  $n_o$  ionizations in order of increasing binding energy. The photoabsorption spectrum has been recorded in the gas phase using both a synchrotron radiation source (5–9.91 eV, 248–125 nm) and electron energy-loss spectroscopy under electric-dipole conditions (5–10.9 eV, 248–90 nm). The (UV) absorption spectrum has also been recorded in solution (4.2–6.36 eV, 292–195 nm). The electronic excitation spectrum appears to be dominated by transitions between  $\pi$  and  $\pi^*$  orbitals in the aromatic ring, leading to the conclusion that the frontier molecular orbitals of furan are affected only slightly on replacement of a H atom by the  $-\text{CH}_2\text{OH}$  group. Additional experiments investigating electron impact at near-threshold energies have revealed two low-lying triplet states and at least one electron/molecule shape resonance. Dissociative electron attachment also shows to be widespread in furfuryl alcohol. © 2003 American Institute of Physics. [DOI: 10.1063/1.1603733]

## I. INTRODUCTION

The furan molecule plays a central role in many fields of chemistry. Like pyrrole and thiophene it is pseudo-aromatic, but it retains properties related to those of the conjugated dienes and this contributes to its versatility in organic synthesis.<sup>1</sup> Compounds incorporating the furan ring are of major importance in pharmaceutical, polymer, and materials science.<sup>2</sup> Recently, furan compounds have also been implicated in environmental and atmospheric chemistry.<sup>3,4</sup> Given

this, it is of interest to explore how the electronic structure of furan is affected on substitution of the ring hydrogen atoms by functional groups. We have already reported on the valence-shell electronic spectroscopy of 2-methylfuran.<sup>5</sup> We now present a comprehensive spectroscopic study on 2-furanmethanol (commonly known as furfuryl alcohol) the derivative obtained by substitution of an H atom of furan by a  $\text{CH}_2\text{OH}$  group (Fig. 1).

As well as being of interest because of its relationship to furan, furfuryl alcohol is important in its own right as a synthetic reagent. Currently, it is widely employed in the production of different kinds of resins and polymers used in coating technology;<sup>6</sup> in fact, potential technological applications make it one of the most important furanic derivatives on the market.<sup>7,8</sup>

The geometric structure of furfuryl alcohol (Fig. 1) has been established from microwave spectroscopy and *ab initio*

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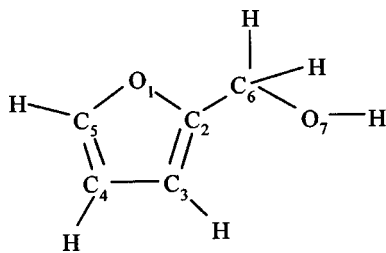


FIG. 1. 2-furanmethanol (furfuryl alcohol), with atom numbering.

calculations.<sup>9</sup> The molecule adopts a skew conformation for  $C_3=C_2-C_6-O_7$  in its two most stable rotamers with dihedral angles of  $105^\circ$  and  $108^\circ$ , respectively. It belongs to the  $C_1$  point group, containing only the identity symmetry element. However, in interpreting its spectroscopy, we emphasize its relationship to furan and so give the observed spectral bands labels from the  $C_{2v}$  point group, appropriate to the corresponding bands in furan. Although not rigorously correct this approach works because the dominant absorption bands in the spectrum appear to result from transitions between perturbed  $\pi$ -orbitals of the parent molecule. This methodology has been previously used successfully in the case of 2-methylfuran, whose spectrum is remarkably similar to that of furan.<sup>5</sup> Also, it is a method generally applied to substituted aromatics compounds.<sup>10</sup>

Little work has been reported on the electronic properties of furfuryl alcohol. This contrasts with furan, whose electronic states have been extensively studied, both by experiment and theory.<sup>11–13</sup> In furan the ground-state electronic configuration ( $^1A_1$  in  $C_{2v}$  symmetry) is  $(\text{core}) \times (2b_1)^2 (1a_2)^2$  where orbitals  $2b_1$  and  $1a_2$  are  $\pi_2$  and  $\pi_3$ , respectively. The lowest unoccupied orbitals are  $\pi_4^*$  ( $3b_1$ ) and  $\pi_5^*$  ( $2a_2$ ). Excited states arising from  $\pi \rightarrow \pi^*$  transitions within this group of orbitals give four singlet  $\pi\pi^*$  excited states, namely two of symmetry  $B_2$  ( $\pi_3\pi_4^*$  and  $\pi_2\pi_5^*$  labeled  $1B_2$  and  $2B_2$ ) and another pair of symmetry  $A_1$  ( $\pi_3\pi_5^*$  and  $\pi_2\pi_4^*$ ).<sup>11</sup> The first optical band of furan spans 5.5–7.2 eV (225–172 nm) with a maximum absorption at 6.04 eV (205 nm). There is agreement that most of the intensity is from excitation of  $1B_2$ . The lower-lying of the two  $^1A_1$  states may also lie within this band, but its oscillator strength is low and it has not yet been established by experiment whether it lies below or above the  $1B_2$  state. Theoretical calculations give conflicting results.<sup>11–13</sup> The second pair of  $A_1$  and  $B_2$  ( $^1\pi\pi^*$ ) states are within an intense absorption band between about 7 and 9 eV. Excitation energies of 7.8 eV (159 nm) and 8.7 eV (143 nm) have been proposed for  $^2A_1$  and  $^2B_2$ , respectively. Sharp Rydberg excitations sit on the two broad valence bands.<sup>11</sup>

In the present studies, we have recorded the electronic [vacuum ultraviolet (VUV)] excitation spectrum of gaseous furfuryl alcohol using a synchrotron radiation source. A high resolution electron energy-loss spectrum (HREELS) has been obtained under conditions which mimic the optical spectrum, and which extend the spectral range of the measurements. Electron energy-loss spectra have also been studied using incident electrons of near-threshold energies. The lowest ionization energies have been measured by high-

resolution photoelectron spectroscopy. Finally, we have determined the UV spectrum of the compound in a solution of cyclohexane.

## II. EXPERIMENT

### A. Photoelectron spectrometer

The photoelectron spectrometer has been described in detail.<sup>14,15</sup> Briefly, He I photons (58.4 nm) are produced by a dc discharge in helium. The spectra were recorded by sweeping a retarding voltage in steps of 1 meV between the ionization chamber and the entrance slit of a  $180^\circ$  hemispherical selector electrostatic analyzer, working in constant pass energy mode. Spectra were corrected for the transmission of the analyzing system. The overall resolution was about 25 meV. The ionization energy scale was calibrated using the xenon peaks ( $^2P_{3/2}$ : 12.123 eV and  $^2P_{1/2}$ : 13.436 eV).<sup>16</sup> The accuracy of the energy measurements is estimated to be  $\pm 0.002$  eV.

### B. Gas-phase VUV absorption apparatus

The photoabsorption spectrum was recorded at the UV1 beam line<sup>17</sup> of the storage ring ASTRID at Århus University, in Denmark. The normal incidence monochromator was operated using the 2000 l/mm grating with an overall resolution (full width at half maximum, FWHM) of better than 0.1 nm. The radiation from the monochromator passed through a  $\text{CaF}_2$  window into a gas cell of length 15 cm. A Baratron capacitance manometer monitored the sample pressure (less than 0.1 mbar), and the intensity of the radiation exiting the cell through a second  $\text{CaF}_2$  window was detected using an UV enhanced photomultiplier tube (Electron Tube Limited). The spectral range extended from about 5 eV (248 nm) to the  $\text{CaF}_2$  cutoff at 9.91 eV (125 nm). This range was covered in sections of 11 nm each, using steps of 0.1 nm; this step was found to be sufficiently small to resolve the structures in the cross section curves. The radiation transmitted through the empty cell ( $I_0$ ) was first recorded over the limited (11 nm) range. Sample was then introduced into the cell and two scans of transmitted radiation ( $I_t$ ) were recorded. The cell was subsequently evacuated and a second ( $I_0$ ) recorded. The mean of each of the of  $I_0$  and  $I_t$  values was used in the Beer–Lambert law to evaluate the cross section  $\sigma$

$$I_t = I_0 \exp(-\sigma N x)$$

where  $N$  is the target gas number density and  $x$  is the path length.

The averaging procedure compensated effectively for decay of the radiation intensity as the storage ring current decayed. Spectra are presented on an energy (eV) abscissa to enable direct comparison with the electron energy-loss data. The accuracy of the cross section is estimated to be  $\pm 5\%$ .

### C. Electron energy loss spectrometer (HREELS)

The instrument used (VG-SEELS 400) has been described in detail elsewhere.<sup>18</sup> In this, an electrostatic electron energy monochromator defines a narrow energy spread about

the mean incident electron energy and a three elements lens focuses the electrons into the collision region. The electron beam intersects the gas beam, which flows through an hypodermic needle, at 90°. The analyzer system is of the same type as the monochromator. Both electron energy selectors work in the constant pass-energy mode. The scattered electron signal is detected by an electron multiplier of the continuous dynode type. The resolution, measured at the FWHM of the peak due to elastically scattered electrons (elastic peak), was about 40 meV. The residual energy of scattered electrons ( $E_r$ ) is related to the impact energy ( $E_i$ ) as follows:  $E_i = E_p + E_r$ , where  $E_p$  is the energy-loss. The elastic peak corresponds to electrons with zero residual energy and hence is used to calibrate the electron energy-loss scale. Accuracy on the energy scale is  $\pm 0.008$  eV. Spectra were recorded for energy-losses between 4.5 and 12 eV at step intervals of 8 meV. The operating pressure was  $1.5 \times 10^{-5}$  mbar during the measurements. The apparatus was used with relatively high incident energy electrons (100 eV) and a scattering angle ( $\theta \sim 0^\circ$ ), such that electric dipole interaction conditions apply and the electron energy loss spectrum is comparable with the photoabsorption spectrum. The inelastic scattered intensity was converted to a relative differential oscillator strength (DOS) distribution, using the method developed previously:<sup>19</sup>

$$\frac{df}{dE} \propto I(E_p) \left\{ \ln \left[ 1 + \left( \frac{\bar{\theta}}{\gamma} \right)^2 \right] \right\}^{-1}$$

and

$$\gamma^2 = \left( \frac{E_p}{2T} \right)^2 \left( 1 - \frac{E_p}{T} \right)^{-1}.$$

$T$  is the incident electron energy,  $E_p$  is the electron energy loss,  $I(E_p)$  is the scattered intensity and  $\bar{\theta}$  is the spectrometer angular acceptance ( $1.25^\circ \pm 0.25^\circ$ ).

To obtain absolute values, the HREELS data must be normalized to a known cross section at a particular wavelength measured in the optical experiment. The cross section may then be calculated from

$$\sigma = 109.75 \frac{df}{dE},$$

where  $\sigma$  is in Mb and  $df/dE$  is in  $\text{eV}^{-1}$ .

Comparison of the HREELS cross section values with those recorded using the synchrotron source provides a test for any systematic error in the optical values arising from the line saturation effect and second-order light from the light source and beam line. These were found to be negligible in this work.

#### D. Trapped electron spectrometer

Near-threshold electron energy loss spectra were recorded in a trapped electron spectrometer which has been described.<sup>20</sup> Briefly, incident electrons emitted from a filament are energy selected by a trochoidal monochromator, which operates through the combined actions of an axial magnetic field and a perpendicular electric field. The energy-selected electrons enter collision region where the electro-

static potentials are such that those scattered electrons whose residual energy,  $E_r \leq eW$  (where  $W$  is the so-called trap well-depth) are trapped and collected along with any stable negative ions formed in dissociative attachment processes. A negative ion current can be identified because it persists when  $W=0$ , because the trajectories of the relatively massive ions are not significantly influenced by the axial magnetic field; ions therefore travel in straight lines from the source and (unless emerging in a forward direction) are intercepted by the collector.

The electron energy loss scale was calibrated with reference to the krypton  $^1P_1$  peak at 10.04 eV.<sup>21</sup>

#### E. Condensed phase UV photoabsorption spectroscopy

Absorption spectra of the chromophore, in solution in cyclohexane at various dilutions, were measured using a Kontron double beam spectrophotometer (Uvikon 941), with the solution in a quartz cuvette (0.4 cm width and 1 cm length, Hellma). Accuracy for molar extinction coefficient is estimated at 30% at the band maximum and that for absorbance measurement at 10%.

#### F. The sample

The furfuryl alcohol, stated purity 99%, was purchased from Acros Organics. The compound is highly hygroscopic and produces a strong azeotrope with water; it was, therefore, handled under a controlled atmosphere of  $\text{N}_2$ . Prior to use in gas phase experiments, the sample was de-gassed by repeated freeze-pump-thaw cycles. For the solution spectra, the cyclohexane solvent was HPLC grade, purchased from Sigma.

### III. RESULTS AND DISCUSSION

#### A. General comments

It has been shown that methyl substitution at position 2 of the furan ring affects the spectrum only slightly shifting the  $\pi\pi^*$  bands to lower energies (by about 0.1 eV) and modifying the intensities, but without introducing any new bands.<sup>5</sup> 2-methylfuran may be regarded as a precursor of furfuryl alcohol, a H atom in the former being replaced by  $-\text{OH}$  to give the alcohol. Also, furfuryl alcohol bears the same relation to furan that benzyl alcohol ( $\text{C}_6\text{H}_5\text{CH}_2\text{OH}$ ) does to benzene; the  $-\text{CH}_2\text{OH}$  group modifies the spectrum of benzene in much the same way as does the methyl group.<sup>22</sup> We, therefore, discuss the present results for furfuryl alcohol together with those for furan and 2-methylfuran.

#### B. The photoelectron spectrum

Figure 2 shows the photoelectron spectrum of furfuryl alcohol compared with those of furan<sup>5,23</sup> and 2-methylfuran<sup>5</sup> in the 8–12 eV ionization energy region. The furfuryl alcohol spectrum contrasts with those of the other two molecules in that three ionization bands are seen rather than two and none shows vibrational fine structure. Vertical ionization energies ( $IE_v$ ) for furfuryl alcohol are 8.880, 10.339, and 10.777 eV, respectively, the last two showing overlapping

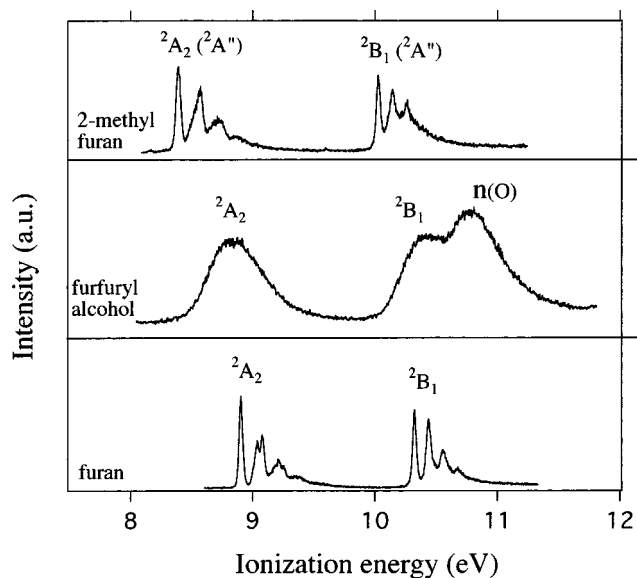


FIG. 2. Comparison of the He I photoelectron spectra of furfuryl alcohol, furan (Refs. 5 and 23) and 2-methylfuran (Ref. 5) in the 8–11.2 eV region.

bands. Considering the expected slight effect of the  $-\text{CH}_2\text{OH}$  group on the ring  $\pi$ -orbitals, we assign the first two ionizations to removal of electrons from  $\pi$ -ring orbitals (Table I). The 10.777 eV band is then attributed to ionization of an oxygen lone pair electron,  $n_o$ . This ionization energy is close to the first  $n_o$  ionization energy in methanol (10.94 eV) and ethanol (10.64 eV).<sup>24</sup> Also, the first  $n_o$  ionization in benzyl alcohol has been attributed to a band observed at 10.61 eV;<sup>25</sup> this last assignment was made from comparative studies on gas and liquid-phase photoelectron spectra and so is considered secure.

Differences between the  $\pi$ -ionization energies of furfuryl alcohol and those in furan may be explained by  $\sigma_\pi/\pi$  hyperconjugation and inductive effects.<sup>26–28</sup> In 2-methylfuran both effects destabilize the ring  $\pi$ -orbitals with a concomitant reduction in ionization energies. The effects are more marked for orbital  $\pi_3(1a_2)$ , in which the electron density is concentrated along  $\text{C}_2\text{--C}_3$  and  $\text{C}_4\text{--C}_5$  bonds, than for  $\pi_2$  where the density is along  $\text{C}_3\text{--C}_4$ . For furfuryl alcohol similar arguments apply, but in this case, the  $-\text{OH}$  group counteracts electron donation from the  $\text{CH}_2$  group. By withdrawing electrons from the ring, OH stabilizes the  $\pi$ -orbitals and hence increases their ionization energies. The net result is that, relative to furan, the  $\pi$ -electron

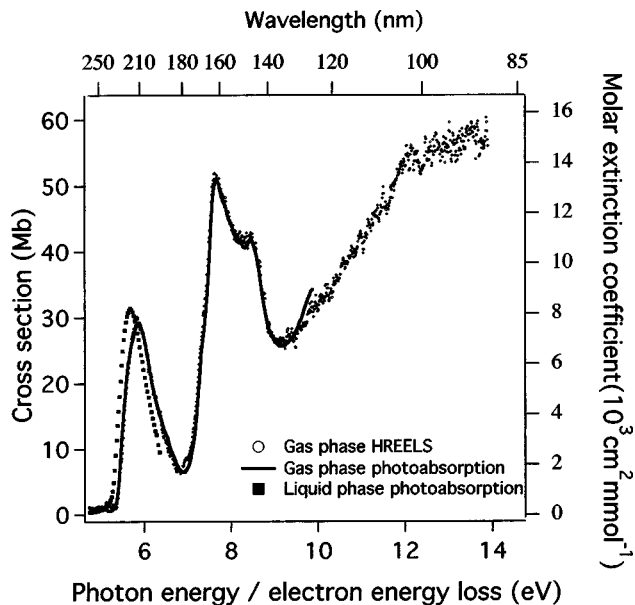


FIG. 3. Comparison of the spectra of furfuryl alcohol: (—) gas phase, VUV photoabsorption; (○○○) gas phase, HREEL; (■■■) solution, UV absorption. The HREELS data were recorded at 100 eV and 0°, converted into differential oscillator strength and normalized to the VUV spectrum at 8.3 eV (149 nm).

ionization energies of furfuryl alcohol are less stabilized than those of the methyl derivative and they fall between those of the other two (Fig. 2, Table I).

Although the effect of substitution on the energies of the  $\pi$ -orbitals of the furan ring appears to be slight, the presence of the  $-\text{OH}$  group has a profound effect on the ionic potential surfaces; in contrast to 2-methylfuran, none of the cationic states survives sufficiently long to show vibrational structure (Fig. 2). This might be due to vibronic couplings and/or dissociation and/or predissociation processes which may occur due to crossings with dissociative electronic states.

It follows that, in the electronic absorption spectrum of the molecule, excitation of a Rydberg-type state (which comprises a distant electron bound to a positive ion core) appears as a broad band (see below).

### C. Singlet excited states

Figure 3 illustrates the gas-phase photoabsorption spectrum (5–9.91 eV), the HREEL spectrum (5–13.9 eV) and an

TABLE I. Vertical ionization energies (eV) of furfuryl alcohol. Comparison with furan and 2-methylfuran. Labeling of the ionic states are made in the  $C_{2v}$  point group. Vertical ionization energies values have been obtained by taking the center of the bands.

Compound	$\text{EI}_1 (^2A_2)$		$\text{EI}_2 (^2B_1)$		References
	Energy	$\Delta$	Energy	$\Delta$	
Furan	9.093	...	10.528	...	a
Furfuryl alcohol	8.880	−0.223	10.339	−0.189	This work
2-methylfuran	8.605	−0.488	10.271	−0.257	b

<sup>a</sup>References 5 and 23.

<sup>b</sup>Reference 5.



TABLE II. Excitation energies (eV) of the lowest energy valence states for furfuryl alcohol, furan, and 2-methylfuran.

States	Compounds		
	Furan	2-methylfuran	Furfuryl alcohol
$^3B_2$	3.97 <sup>a</sup>	3.85 <sup>b</sup>	3.9 <sup>c</sup>
$^3A_1$	5.2 <sup>a</sup>	5.1 <sup>b</sup>	5.1 <sup>c</sup>
$1^1B_2$	6.06 <sup>d</sup>	5.95 <sup>c</sup>	5.87 <sup>c</sup>
$1^1A_1$	7.8 <sup>d</sup>	7.7 <sup>c</sup>	7.65 <sup>c</sup>
$2^1B_2$	8.7 <sup>d</sup>	8.4 <sup>c</sup>	8.5 <sup>c</sup>
$\Delta(^1B_2-^3B_2)$	2.09	2.1	1.97

<sup>a</sup>Reference 31.<sup>d</sup>Reference 11.<sup>b</sup>Reference 32.<sup>c</sup>Reference 5.<sup>e</sup>This work

optical absorption spectrum recorded for a solution in cyclohexane (4.2–6.36 eV). Where they overlap, the VUV and HREEL spectra are concordant. The first absorption band in the gas-phase spectra is reproduced in solution, with a slight red shift in energy;<sup>10</sup> peak maxima are at 5.87 (211 nm) and 5.69 eV (218 nm) in gas-phase and solution respectively. This behavior is similar to that observed for the methyl derivative (energy shift = −0.1 eV)<sup>29</sup> and is consistent with the shift expected for excitation of a  $^1\pi\pi^*$  state.<sup>10</sup> A recently reported  $E_{\text{max}}$  of 4.96 eV for furfuryl alcohol in solution can now be discounted as being too far adrift from the gas-phase maximum.<sup>30</sup>

As predicted above from empirical considerations, the broad spectrum resembles those of furan and 2-methylfuran, stripped of their Rydberg fine structure. The electronic spectrum has the appearance of a valence-excitation spectrum dominated by transitions between  $\pi$  and  $\pi^*$  orbitals. Assignments for these then follow by analogy with furan. Thus, we suppose the first  $\pi\pi^*$  band to derive most of its intensity from excitation of (in  $C_{2v}$  symmetry) the  $1^1B_2$  state,  $E_{\text{max}} = 5.87$  eV (235 nm); the  $1^1A_1$  state is also within this band but is too weak to be identified. The intense peak,  $E_{\text{max}} = 7.65$  eV, 162 nm, is assigned to excitation of state  $2^1A_1$  with  $2^1B_2$  at 8.5 eV (146 nm). These data are compared with those for furan and 2-methylfuran in Table II.

We turn now to excitation of Rydberg states. For a pure Rydberg state, the excitation energy,  $E_{\text{ex}}$  is given by the Rydberg expression:  $E_{\text{ex}} = IE - R/(n - \delta)^2$  where  $IE$  is the ionization energy of the excited electron,  $n$  is the principle quantum number of the upper orbital (here  $n \geq 3$ ) and  $\delta$  is the quantum defect. For  $s$ -type states in furan,  $\delta \sim 0.85$  and with this value for furfuryl alcohol, the Rydberg state  $\pi_3 3s$  is predicted to lie near 5.9 eV. However, because it is symmetry-forbidden in furan, it is likely to have a low oscillator strength in furfuryl alcohol and so not to distort the first absorption band. Rydberg states of type  $\pi_3 3p$  are expected between 6.4 and 6.8 eV. In fact, the full width at half maximum (FWHM) of the first band is *broad*er in the gas phase than in solution. As Rydberg states are suppressed in the condensed phase,<sup>10</sup> we ascribe the broadening of the gas-phase absorption to excitation of  $p$ -type Rydberg states. Similarly, a weak bulge on the rising side of the second band around 7.3 eV coincides with the predicted excitation energy for  $\pi_3 3d$  Rydberg states.

TABLE III. Oscillator strength for furfuryl alcohol bands.

Energy region (eV)	Optical oscillator strength	
	Photoabsorption	HREELS
5.22–6.89	0.239	0.242
6.89–8.31	0.435	0.448
8.31–9.12	0.246	0.251
9.12–13.9	...	1.962

Absolute excitation cross sections for the two optical bands (Fig. 3) are 29 and 52 Mb, respectively. These are close to corresponding values measured for 2-methylfuran (30 and 48 Mb, respectively); for the latter, Rydberg-excited states could be positively assigned.<sup>5</sup> Absolute oscillator strengths for furfuryl alcohol, estimated from both the VUV and HREEL spectra, are tabulated in Table III. Agreement between the two data sets is good showing that the optical spectra are free from the line saturation effects or errors due to second-order radiation.

#### D. Triplet excited states

Figures 4(a) and 4(b), show data recorded in the trapped electron spectrometer for residual electron energies of  $\sim 0.15$  and 0.35 eV, respectively; in each case, the signal contains a contribution from negative ions as well as scattered electrons (see below), but electrons predominate. In Fig. 4(c), the negative ions have been subtracted out, leaving a spectrum of scattered electrons whose residual energy is about 0.35 eV. For comparison, the HREEL spectrum recorded at 100 eV and  $0^\circ$  is included in 4(d).

In analyzing this data, we consider first electron energy-loss processes leading to electronically excited states. The data shows that most important of these are two triplet excited states, positioned at about 3.9 and 5.1 eV, respectively. By analogy with furan, they are assigned as  $^3\pi\pi^*$  states,  $^3B_2$  and  $^3A_1$ , in that energy order; the corresponding energies in furan are 3.97 and 5.2 eV, respectively (Table II).<sup>31</sup> The singlet–triplet splitting for  $^1,^3B_2$  is then 1.97 eV, which is close to the corresponding values in furan and 2-methylfuran<sup>32</sup> (Table II). In furan the  $^1,^3B_2$  states are each believed to result from a simple highest occupied molecular orbital (HOMO)→lowest unoccupied molecular orbital (LUMO) transition.<sup>11–13,33</sup> As a singlet–triplet splitting is determined by the exchange interaction between the two participating orbitals,<sup>34</sup> it may be inferred that the spatial overlap between the two  $\pi$  molecular orbitals is not changed very much upon substitution. This adds credence to the view that the  $\text{CH}_2\text{OH}$  and  $\text{CH}_3$  groups have only a slight effect on the frontier orbitals of the furan ring.

There is a maximum in the energy-loss spectra at about 6 eV [Fig. 4(d)], close to that of the first observed optical band, but energy-losses detected at about 7 eV [Fig. 4(c)] are absent from the optical spectrum. Additional experimental work will be required in order for these to be assigned.

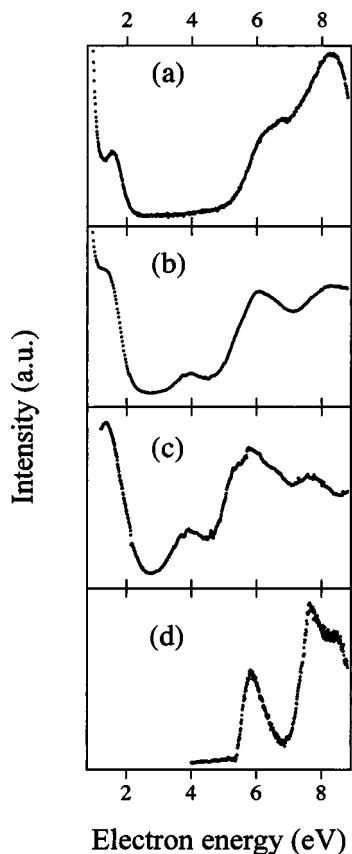


FIG. 4. Electron energy loss spectra of furfuryl alcohol (a)  $E_r \sim 0.15$  eV; (b)  $E_r \sim 0.35$  eV (both contaminated with negative ions); (c) electron only signal,  $E_r \sim 0.35$  eV; (d) 100 eV  $0^\circ$  HREEL spectrum.

### E. Electron-molecule resonant processes

An energy-loss process visible around 1.6 eV in the spectra of Fig. 4(a) is ascribed to vibrational excitation of the neutral molecule by formation and subsequent autoionization of a short-lived negative ion. This anion also decays by dissociation with the extra electron attaching to one of the dissociative fragments (dissociative electron attachment, DEA). This explains the negative ion signal collected at around 2 eV (Fig. 5). We suppose the common intermediate to be the so-called shape resonance resulting from trapping of the incident electron in the lowest unoccupied  $\pi^*$  molecular orbital,  $3b_1^*$ . The present technique does not allow for the

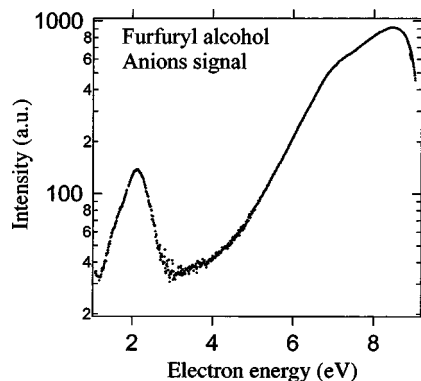


FIG. 5. Negative ion signal for furfuryl alcohol.

accurate determination of the electron attachment energy, so we cannot comment on subtle effects of the substituent on the energies of the unoccupied molecular orbitals, but our estimate for the attachment energy is around 2 eV. The corresponding value for furan is 1.76 eV,<sup>35,36</sup> however in furan the dissociative attachment channel is not observed.

As the incident electron energy is increased additional DEA processes are revealed, resulting in the continuous production of negative ions (Fig. 5). The threshold for these is about 3 eV which is close to the expected attachment energy for occupation of orbital  $2a_2$ ,  $\pi_5^*$  (3.15 eV in furan).<sup>36</sup> The alcohol group is probably implicated in the higher electron attachment processes as dissociative attachment to methanol has been observed leading to production of, mainly,  $H^-$  and  $O^-$  centered around attachment energies of 6.5, 8.5, and 10.5 eV, respectively.<sup>37</sup>

### IV. CONCLUDING COMMENTS

We have made a range of spectroscopic measurements on 2-furanmethanol (furfuryl alcohol), all of which may be interpreted on the assumption that substitution of a ring H by the  $CH_2OH$  group has only a slight effect on the frontier orbitals of the furan system. This statement applies to the photoelectron spectrum, which has given information on the highest occupied  $\pi$ -molecular orbitals; electron impact studies which have yielded information on the normally unoccupied  $\pi^*$  orbitals; and to electronic excitation spectra which have revealed  $\pi \rightarrow \pi^*$  transitions, including some which are spin-forbidden. All of the spectra may, therefore, be interpreted by analogy with furan, about which a great deal is known. A major difference between furan and furfuryl alcohol is the absence of vibrational fine structure in any of the spectra of the latter. The propensity for bond rupture exists also in its interaction with electrons of low energy, which in contrast to furan, leads to widespread dissociative electron attachment in furfuryl alcohol.

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