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Lowest energy triplet states of furan, studied by high resolution electron energy loss spectroscopy

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Abstract

The excitation spectrum of furan has been recorded between 3 and 6.2 eV by high resolution electron energy loss spectroscopy at 30 eV incident electron energy and scattering angles of 10° and 25°. The lowest energy singlet–triplet transitions are confirmed to be responsible for two bands centred at 3.97 eV ($^3B_2$) and 5.15 eV ($^3A_1$), respectively. Vibrational structure is resolved for the first time in the $^3A_1$ band and its analysis has provided identification of the excited state normal modes and their energy. (Int J Mass Spectrom 205 (2001) 163–169) © 2001 Elsevier Science B.V.

Keywords: Furan; Electron energy loss spectroscopy

1. Introduction

This work is concerned with the valence electron spectroscopy of furan, a five member aromatic heterocycle. Since the first investigations in the 1940s [1,2], its electronic spectrum has been studied experimentally [3–11] and theoretically [11–17]. Most of the features due to the singlet–singlet transitions involving the occupied valence molecular orbitals $2b_1$ and $1a_2$ are now interpreted. Nevertheless, discrepancies still remain between the four most recent theoretical articles [11,15–17] concerning the precise energy location and the symmetry description of some excited states. The lack of a clearly distinguishable vibrational structure arising in the two lowest π–π^* valence transitions has been pointed out [16,17].

In the 3–5.6 eV region, two broadbands have been reported by electron energy loss spectroscopy (EELS) with a resolution of 111 meV [4,5] and by near threshold electron excitation using the trapped electron method [6,11]. The angular dependence of their differential cross section (DCS) has indicated that they could be due to the lowest energy singlet–triplet transitions [4,5]. These conclusions were confirmed by calculations [11–14,16] and the first band at 3.97 eV was assigned to the transition to $^3B_2$ and the second one at 5.2 eV, to $^3A_1$.

One of the particularities of EELS, the spectroscopic method used in this study, lies in the fact that each excitation process is characterised by a specific energy and angular dependence of its DCS. At fixed excitation energy and scattering angle, the ratio of the

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Dedicated to Professor Aleksandar Stamatovic on the occasion of his 60th birthday.

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relative intensities of two spectral peaks in the EELS spectrum is equal to the ratio of the DCS of the corresponding excitations. It is then possible to significantly enhance some transitions relative to others simply by varying the incident electron energy and/or the angle of detection. As the angular DCS of spin-forbidden transitions is nearly isotropic, unlike that of spin-allowed processes, EELS allows observation and identification of the triplet states of organic molecules.

We report in this article data on the electronic excitation spectrum of furan in the region of 3–6.2 eV. Electron energy loss spectroscopy has been used with 30 eV incident electrons and scattering angle of 10°, that is where spin-allowed transitions are preferred, and also at larger angle (25°) to get information on the lowest energy triplet states. The spectral region corresponding to these transitions is reported for the first time at high resolution (31 meV), allowing new features to be resolved.

2. Experiment

The VG-SEELS 400 instrument used has been described in detail elsewhere [18–20]. Briefly, a 150° hemispherical-sector electrostatic electron energy monochromator fitted with a three element lens produces a collimated electron beam, defines a narrow energy spread about the mean energy and focuses the electrons into the collision region. The electron beam intersects the gas beam, which flows through an hypodermic needle at 90°. The analyser system is of the same type as the monochromator and is rotatable from 0° to 120° around the forward direction. Both electron energy selectors work in the constant pass-energy mode. The signal is detected by an electron multiplier of the continuous dynode type. The electron energy loss spectrum was recorded with steps of 8 meV and a resolution of 31 meV. The operating pressure was 1.5×10^{-5} mbar with a base pressure of 10^{-8} mbar. The apparatus was used with an electron energy of 30 eV and at scattering angles of 10° and 25°. Calibration of the electron energy loss scale was made with the elastic peak as zero of the scale.The sample provided by Aldrich Chemical Ltd. has a purity of +99% and, prior of use, was degassed by repeated pump–thaw cycles.

Table 1
Wave number, energy, and description of the normal vibrational modes of the A_1 symmetry of furan in its electronic ground state; ν means stretching vibration and δ bending vibration (from [21]).

Assignation	Wave number (cm^{-1})	Energy (eV)	Description
$\nu_1(a_1)$	3167	0.393	ν_{CH}
$\nu_2(a_1)$	3140	0.389	ν_{CH}
$\nu_3(a_1)$	1491	0.185	ν_{ring}
$\nu_4(a_1)$	1384	0.172	ν_{ring}
$\nu_5(a_1)$	1140	0.141	ν_{ring}
$\nu_6(a_1)$	1066	0.132	δ_{CH}
$\nu_7(a_1)$	995	0.123	δ_{CH}
$\nu_8(a_1)$	871	0.108	δ_{ring}

3. Results and discussion

Furan belongs to the C_{2v} point symmetry group in its electronic ground state. The valence shell configuration is: $2b_1(\pi_2)^2\, 1a_2(\pi_3)^2$ giving a Xtilde; $^1A_1$ ground state. The lowest energy unoccupied π type molecular orbitals are predicted [11–17] to be $3b_1(\pi_4{}^*)^0\, 2a_2(\pi_5{}^*)^0$. The molecule possesses 21 normal vibrational modes of which 8 are of A_1 symmetry (Table 1). The description of the normal modes used here is taken from Motte-Tollet et al. [21]. The two lowest energy electronic transitions $(1a_2)^2 \rightarrow (1a_2)^1 (3b_1)^1$ and $(2b_1)^2(1a_2)^2 \rightarrow (2b_1)^1(1a_2)^2(3b_1)^1$ lead to the states $^{3,1}B_2$ and $^{3,1}A_1$, respectively. The 3–6.2 eV EEL spectrum, shown in Fig. 1, was recorded at 30 eV and 10°, that is under excitation conditions where symmetry and spin allowed transitions are preferred. It exhibits a broad band centred around 6 eV, that has been proposed to hold the contributions from the transitions to $^1A_1$ and $^1B_2$ [11–17]. Below 5.5 eV, two bands of quite low intensity are observable. Fig. 2 displays the spectrum recorded at 30 eV and 25°. The 6 eV band still dominates the spectrum. But the two less intense features have a much larger relative intensity than in the 30 eV, 10° spectrum and are measured to be centred at 3.97 and 5.2 eV. They were reported previously and assigned to spin-forbidden transitions [4–6,11].

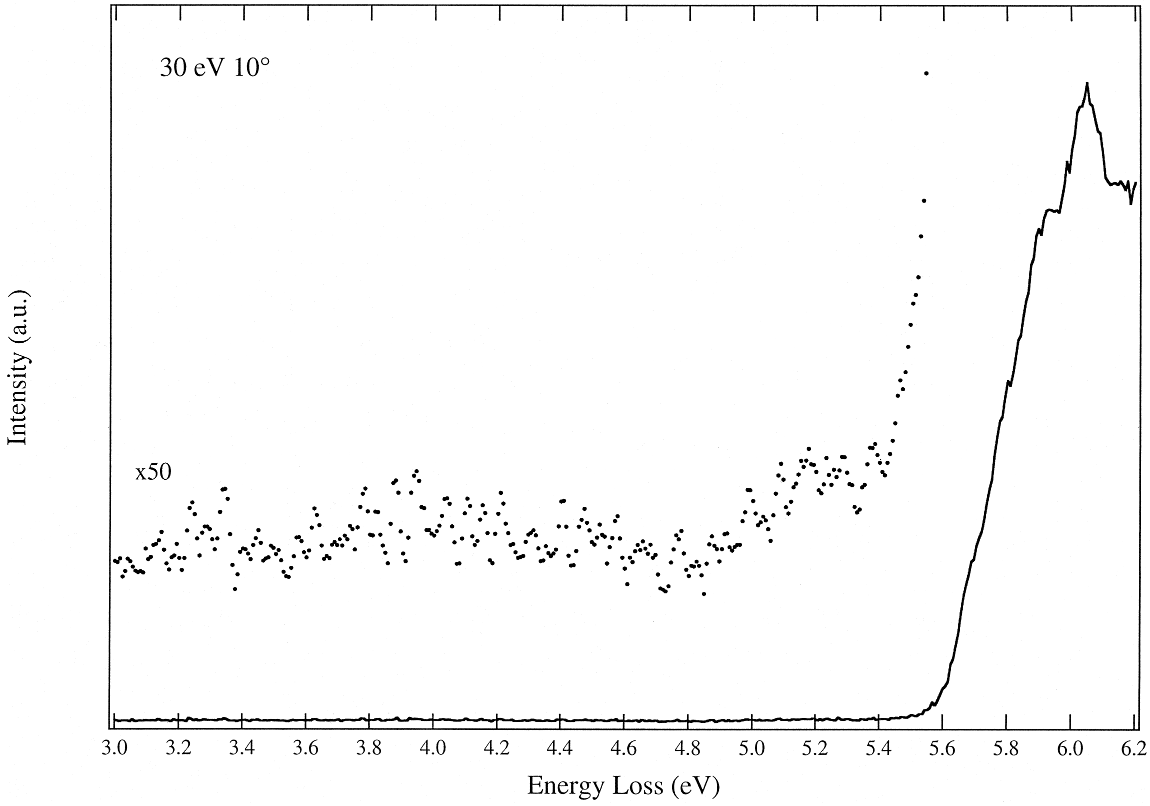

Fig. 1. Electron energy loss spectrum of furan from 3 to 6.2 eV recorded at 30 eV, 10°.

Fine features are observed in the 5.2 eV band but not in the first one.

3.1. $\tilde{X}\ {}^1A_1 \rightarrow {}^3A_1$ transition

The band due to the ${}^3A_1$ excitation extends from 4.74 eV to at least 5.55 eV (Fig. 2). It shows a rather well resolved vibrational structure, reported here and better seen in the enlargement given in the inset of Fig. 3. The spectrum exhibits two weak features at 4.74 and 4.84 eV and four relatively intense peaks at higher energy, for which fine features of much lower intensity are observed as shoulders. The assignment of the 0–0 transition to the very weak feature located at 4.84 eV (Fig 3, Table 2) allows one to analyse the structure in terms of three progressions. The most intense progression has four members and a vibrational energy spacing ranging from 0.128 to 0.136 eV (see Table 2). Within our energy resolution, we suggest to assign it to excitation of the modes $\nu 5$ (ν_{ring}) and/or $\nu 6$ (δ_{CH}) and/or $\nu 7$ (δ_{CH}), their energies being close to those in the ground state which are 0.141, 0.132, and 0.123 eV, respectively (Tables 1 and 2). It will be represented by the notation $n\nu_{5,6,7}$, with $n = 1, 2, 3$, and 4. The second progression is less intense than the first one, the features appearing only as shoulders on the bands of the main progression. Three members with an energy spacing ranging from 0.184 to 0.192 eV are observed and tentatively assigned to excitation of the modes $\nu_{3,4}$, since the energies are close to those in the ground state of $\nu_3(\nu_{\mathrm{ring}})$ (0.185 eV) and of $\nu_4(\nu_{\mathrm{ring}})$ (0.171 eV), respectively. For the third progression, a single member may be observed as a weak shoulder on the 5.22 eV band (Fig 3). It is located at 0.336 eV from the 0–0 transition and tentatively assigned to excitation

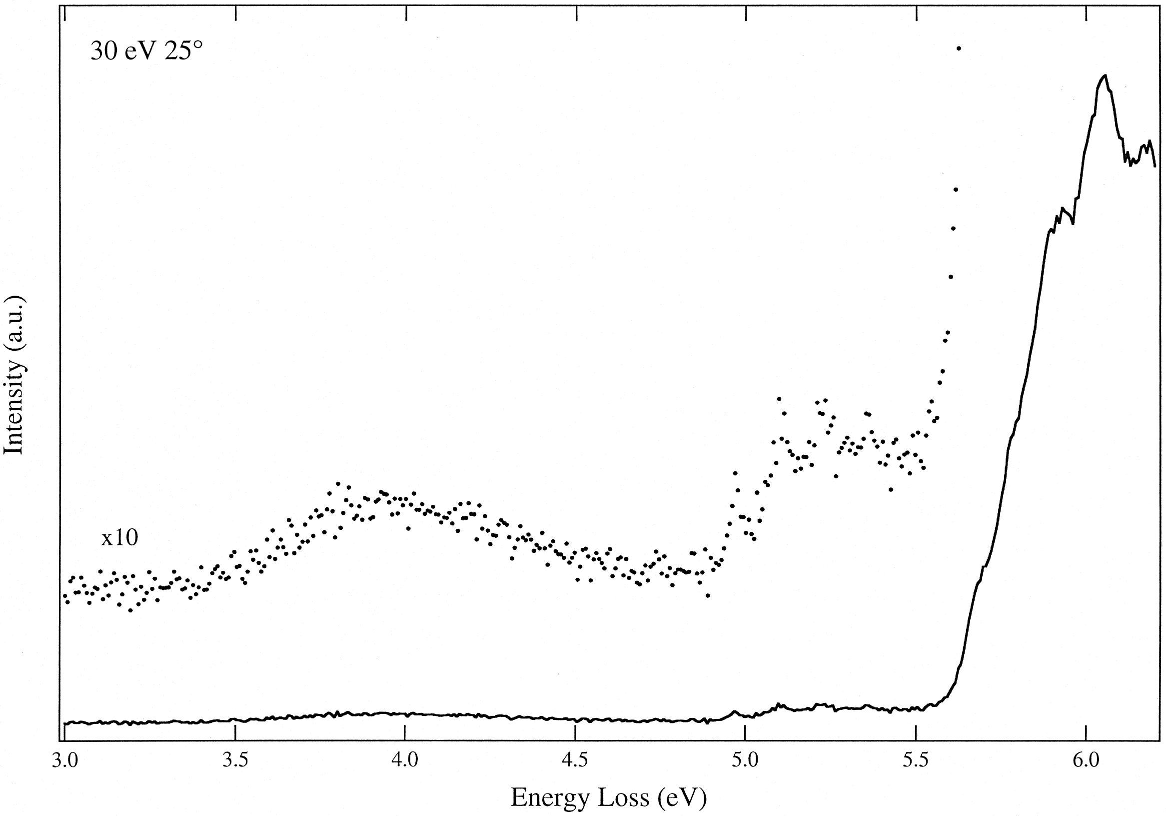

Fig. 2. Electron energy loss spectrum of furan from 3 to 6.2 eV recorded at 30 eV, 25°.

of $1\nu_{1,2}(\nu_{CH})$, this value being consistent with those in the ground state (Tables 1 and 2). The weak feature located at 0.104 eV below the electronic origin (Fig. 3) may be attributed to a hot band with excitation of $1\nu_8$ (δ_{ring}), the energy spacing being very close to the ν_8 value of 0.108 eV in the ground state.

3.2. $\tilde{X}\,^1A_1 \rightarrow {}^3B_2$ transition

The spectral region attributed to the $^3B_2$ transition is shown in Fig. 2. The band is much broader than the $^3A_1$ one, asymmetric on the high energy side and seems structureless. It extends from 3.4 to 4.65 eV with a maximum at 3.97 eV. The apparent lack of vibrational structure and the broadness suggest a rather short lifetime for the excited state which might be due to intersystem crossing and/or to rapid dissociation process [22]. A recent study of the ultraviolet photodissociation of furan probed by tunable synchrotron radiation [23] has reported data on two closed shell channels and on a radical channel decomposition observed by photolysis at 193 nm (6.42 eV) with a dye laser and detection of the fragments using the time-of-flight method. The anisotropy parameter measurements lead to conclude that the cleavage into the radical fragments, C_3H_3 and HCO, occurs rapidly, in at most a few rotational periods and that it is the only dissociation that takes place fast. The photolysis of the molecule took place through excitation of a 3*p* Rydberg molecular orbital assigned to a $^1B_2$ state by Palmer et al. [11], or to a $^1B_1$ state [16,17]. The dissociation limit should be around 4.2 eV for the radicals in their ground states [23,24] and correlated to an excited state potential energy surface [23,25]. Taking into account these data and the location of the $^3B_2$ spectral band in the 4 eV region,

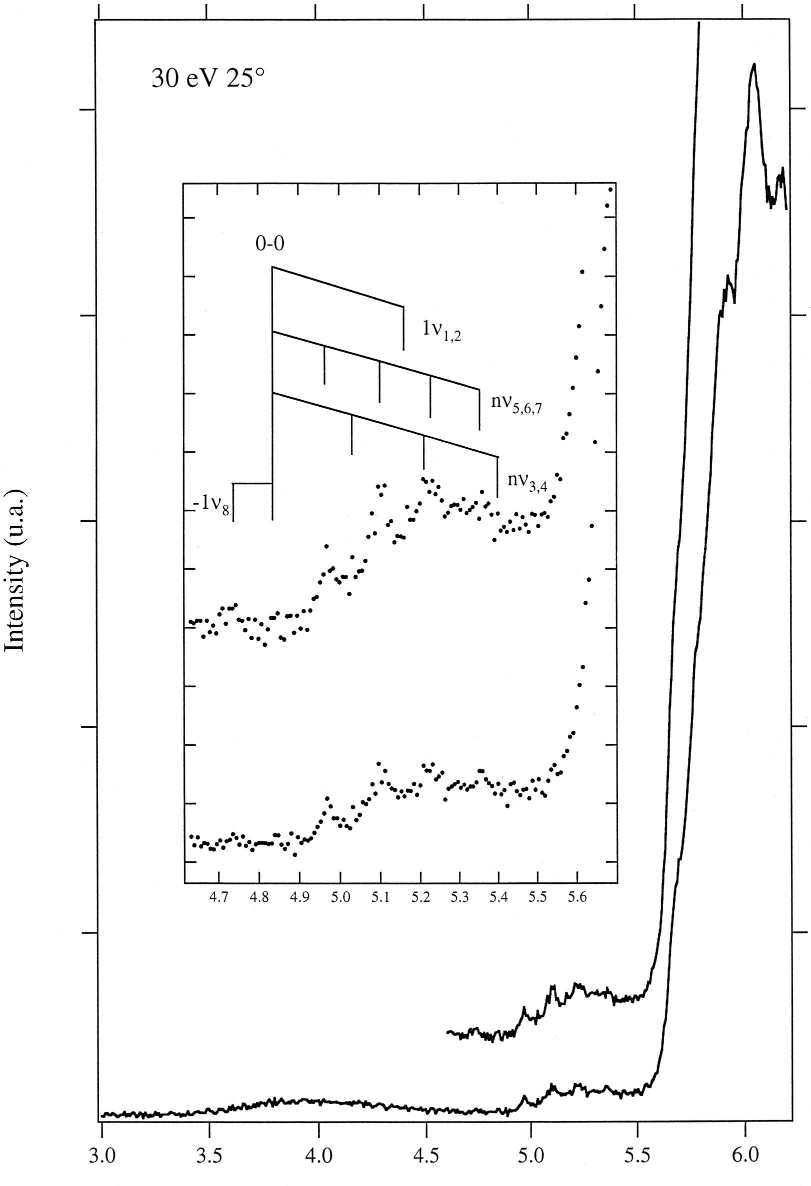

Fig. 3.30 eV, 25° electron energy loss spectrum in the 3–6.2 eV region. Inset: the 4.6–5.7 eV region with an improved signal/noise ratio due to a number of spectra much larger than for the 3–6.2 eV spectrum presented on the same figure.

this state might be correlated to the fast radical dissociation. This is consistent with the fact that no fluorescence and no phosphorescence have been observed for furan [26]. Our experimental results do not allow us to suggest if the state is completely repulsive or has a shallow well.

4. Concluding remarks

The electronic excitation spectrum of furan has been investigated in the 3–6.2 eV region using the high resolution electron energy loss spectroscopy. We report new data on the energies of the transi-

Table 2
Energies and vibrational assignments for the $\tilde{X}\ ^1A_1 \rightarrow {}^3A_1$ transition; all energies are given in electron volts; Data for the electronic ground state are taken from [21] and references therein

Energy	Assignment	Vibrational energy		Description
		$^3A_1$	$\tilde{X}\ ^1A_1$	
4.736	$1\nu_8$	−0.104	0.108	δ_{ring}
4.84	0–0	· · ·	· · ·	· · ·
4.968	$1\nu_{5,6,7}$	0.128	0.141/0.132/0.123	$\nu_{ring}/\delta_{CH}/\delta_{CH}$
5.032	$1\nu_{3,4}$	0.192	0.185/0.172	ν_{ring}
5.104	$2\nu_{5,6,7}$	0.264		· · ·
5.176	$1\nu_{1,2}$	0.336	0.393/0.389	ν_{CH}
5.216	$2\nu_{3,4}$	0.376		· · ·
5.240	$3\nu_{5,6,7}$	0.400		· · ·
5.368	$4\nu_{5,6,7}$	0.528		· · ·
5.400	$3\nu_{3,4}$	0.560		· · ·
5.496	$5\nu_{5,6,7}$	0.656		· · ·

tions to the lowest energy $^3B_2$ and $^3A_1$ triplet states. Vibrational progressions associated with the second of them are reported for the first time. No apparent vibrational structure is observed for the first one. Due to its location in the 4 eV region, the $^3B_2$ state might be correlated to the fast radical dissociation in C_3H_3 and HCO, of which limit has been reported around 4.2 eV [23,24]

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