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Chemical Physics 336 (2007) 136–142

Chemical Physics

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Resonance-enhanced multiphoton ionization of jet-cooled 2-methylfuran

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Received 23 March 2007; accepted 25 May 2007

Abstract

Mass-resolved, resonance-enhanced multiphoton ionization (REMPI) spectra of jet-cooled 2-methylfuran have been measured in various spectroscopic regions (visible and UV ns dye laser). The results have been interpreted as two-photon resonances and as three-photon resonances to the 3d Rydberg manifold chiefly. The 3d $^1A_1 \leftarrow (\tilde{X})A_1$ transition, located at 56,360 cm^{-1}, is the strongest one in the $(2+1)$ REMPI spectrum and has a discrete vibrational structure. The vibrational analysis has been performed. The three-photon resonance spectrum tracks the 3d VUV absorption spectrum. The strongest transition in this case is the 3d $^1B_2 \leftarrow (\tilde{X})A_1$ transition located at 56,013 cm^{-1}. The transition to the 3s A_2 Rydberg state has been detected at 44,018 cm^{-1} $(3+2$ REMPI spectrum).

Keywords: Methyl furan; Rydberg transitions; VUV absorption; REMPI; MP2; CASSCF

1. Introduction

The interpretation, both qualitatively and quantitatively, of the furan (C_4H_4O) electronic spectrum has been an experimental and theoretical challenge. The presence of a number of Rydberg transitions, which overlap some broad and diffuse bands assumed to arise from π–π* valence type excitations, complicates the spectrum [1–3]. Resonance-enhanced multiphoton ionization (REMPI) is a powerful spectroscopic technique to reveal the Rydberg transitions [4,5]. The recent REMPI study by Ridley et al. [6] gives an inclusive picture of the Rydberg states of furan. The assignment of the Rydberg transitions of furan is now well documented experimentally [6]. The electronic structure and spectroscopy of furan has attracted high attention because it is the simplest unsaturated five-member heterocyclic pseudo-aromatic molecule.

The derivatives of furan are also important structural units in organic chemistry, molecular biology and material science. In the present work we have applied the REMPI technique to study the Rydberg states of 2-methylfuran (MFU), a simple derivative of furan. MFU (C_5H_6O) has one methyl group in *ortho*-position to the oxygen atom It is well established that, by selecting the number of resonant photons (two- or three-photons) and the polarization of the exciting light (linear, circular), the symmetry of the transition can be determined. *Ab initio* calculations of the vibrational normal modes for neutral MFU and its cation have been performed and the predictions have been taken into consideration for the vibrational analysis of the Rydberg states. Nyulaszi [7] investigated the vapor-phase and solution spectra of MFU in the near UV region (245–195 nm). An essential experimental study of the excited electronic levels of MFU has been carried out by Giuliani et al. [8]. They measured the UV–VUV absorption (248–125 nm region) in absolute values and found intense π–π* transitions and Rydberg series converging to the first and second ionization energies. The presence of the Rydberg

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doi:10.1016/j.chemphys.2007.05.030

states complicates the spectrum but the inclusion of high-resolution electron energy loss spectroscopy (HREELS) contributed in the interpretation of the observed absorption bands [8].

2. Computational details

All calculations were performed by means of the GAUSSIAN 03 [9] suite of programs. Electronic energy calculations, along with optimized geometries of neutral S_0 and cationic D_0 MFU, were initially performed by employing the restricted, closed shell second order Møller–Plesset perturbation theory, RMP2(full) [10], for the neutral MFU, whereas the unrestricted, open shell second order Møller–Plesset perturbation theory, UMP2(full) [10], was employed for the cation. Due to spin contamination, energy values were annihilated and the projected ones resulted, i.e. PMP2//UMP2. The cc-pVTZ [11] basis set was used. Consecutively, the CASSCF method was employed at the same basis set, denoted as CAS(8, 7) for the neutral S_0 MFU and CAS(7, 7) for the cationic D_0 MFU. The active space chosen for the CAS/cc-pVTZ calculations contains the oxygen π lone pair, the two occupied π and two unoccupied π^* orbitals of the MFU ring as well as the σ and σ^* orbitals of the carbon–oxygen bond. Furthermore, vibrational harmonic frequencies were calculated at both the MP2(full)/cc-pVTZ and the CAS/cc-pVTZ levels of theory.

3. Experimental procedure

The REMPI apparatus has been described previously [12]. Briefly, 2-methylfuran (Aldrich, 99% purity) seeded in Ar (2.0–3.5 atm) was expanded into a vacuum chamber through a pulsed valve of 0.50 mm orifice diameter. The supersonic molecular beam was intersected, in the extraction region of a Wiley–McLaren type TOF mass spectrometer, by the laser beam at a distance ~4 cm from the orifice. The ~4 ns laser light was produced by a Nd:YAG pumped dye laser (Lambda Physik, Scanmate 2EC-400). Various dye solutions (and BBO doubling crystals) have been used to generate the exciting laser light. The laser light was focussed on the molecular beam with an $f = +10$ cm lens. The parent ion current or a fragment ion current was measured as a function of the laser wavelength and the results were interpreted as (2 + 1) or (3 + 1) or (3 + 2) REMPI spectra. Some representative laser-induced mass spectra are given in Appendix A (Supplementary data).

4. Results and discussion

4.1. Optimized geometries and the vibrational frequencies in the S_0 neutral state and in the D_0 cationic state

The theoretical results show that both neutral and cationic MFU have a planar C_s equilibrium geometry. Table 1 contains the optimized *ab initio* at the MP2(full)/cc-pVTZ and CAS/cc-pVTZ levels of theory equilibrium geometry parameters for both species. The numbering of the atoms is given in Fig. 1. MFU exhibits distinct conformational preference: One of the methyl C–H bonds is in the plane of the furan ring which forms a plane of symmetry (eclipsed conformation). This bond is *trans* to the C–O bond. Upon ionization, the removal of a π electron does not change this conformation. The main changes (upon ionization) are the considerable decrease of the 3C–4C bond and the increase of the 2C–3C and 4C–5C bonds (Table 1). The MP2 and CAS results are conflicting for the O–2C and O–5C bonds: according to the MP2 calculations, the O–2C bond decreases by 0.037 Å and the O–5C bond increases by 0.004 Å upon ionization. The CAS calculations elongate the O–2C bond by 0.021 Å and shorten the O–5C bond by 0.061 Å upon ionization.

The *ab initio* calculated vibrational frequencies for neutral and cationic MFU are presented in Table 2. The experimental frequencies, for the neutral molecule [13], are

Table 1
Equilibrium geometrical parameters (MP2(full)/cc-pVTZ and CAS/cc-pVTZ) for neutral (S_0) and cation (D_0) 2-methylfuran

Distance	C_5H_6O, S_0 (Å)		$C_5H_6O^+$, D_0 (Å)		Angle	C_5H_6O, S_0 (°)		$C_5H_6O^+$, D_0 (°)	
	MP2	CAS	MP2	CAS		MP2	CAS	MP2	CAS
O–2C	1.357	1.345	1.320	1.366	5C–O–2C	107.2	107.0	107.2	108.1
2C–3C	1.358	1.354	1.410	1.390	O–2C–3C	110.4	111.1	111.1	109.9
3C–4C	1.421	1.438	1.369	1.376	2C–3C–4C	106.0	105.6	105.6	106.3
4C–5C	1.361	1.351	1.408	1.476	3C–4C–5C	106.7	106.6	107.0	106.4
O–5C	1.359	1.376	1.363	1.315	4C–5C–O	109.7	109.7	109.0	119.3
5C–6C	1.475	1.488	1.452	1.476	O–5C–6C	116.7	116.7	117.4	119.1
6C–7H	1.084	1.081	1.081	1.078	5C–6C–7H	109.5	109.9	110.7	110.7
6C–8H	1.086	1.084	1.089	1.084	8H–6C–9H	108.0	108.0	107.0	107.9
6C–9H	1.086	1.084	1.089	1.084	7H–6C–8H	108.4	108.4	109.9	109.9
2C–2H	1.070	1.066	1.074	1.067	O–2C–2H	116.0	116.1	116.8	116.0
3C–3H	1.071	1.065	1.072	1.068	2C–3C–3H	126.1	126.2	125.4	125.4
4C–4H	1.071	1.068	1.072	1.068	5C–4C–4H	125.7	126.2	124.9	124.7

Dihedral angle in S_0: 9H–6C–5C–O = –(8H–6C–5C–O) = 60.2°/60.1° (MP2/CAS).
Dihedral angle in D_0: 9H–6C–5C–O = –(8H–6C–5C–O) = 58.6°/58.9°(MP2/CAS).
The numbering of the atoms is given in Fig. 1.