

Investigation of the electronic vibrational structure of furan by REMPI

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Abstract

Resonance-enhanced multiphoton ionization (REMPI) has been applied to detect the hot bands as well as the cold bands of the $1a_2 \rightarrow 3d_{xy}(^1A_1)$ Rydberg transition of furan (jet-cooled, mass-analyzed). Based on the unambiguous assignment of the hot bands, a complete vibronic analysis is given for the cold bands of this transition (up to 4600 cm^{-1} above the origin). This analysis can be used for the interpretation of the vibrational structure in the \tilde{X}^2A_2 photoelectron band. The energy ordering of the five 3d Rydberg states is $1A_2 \approx 2A_2 < A_1 < B_1 < B_2$. It is also shown that neutral CH is produced in the UV laser multiphoton photodecomposition of furan.

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1. Introduction

Furan (C_4H_4O) is a planar (C_{2v} symmetry) unsaturated five-member heterocyclic pseudo-aromatic molecule, which appears as a fundamental unit in many biological molecules. Its electronic spectrum has been investigated several times since the early measurements of Pickett [1] and Price and Walsh [2]. The absorption spectrum starts at $E > 5.51\text{ eV}$ as a broad band. The onset of the Rydberg transitions is at 6.472 eV , giving sharp peaks superimposed on the valence continuum [1–5]. The vibrational activity of the Rydberg transitions complicates the interpretation of the absorption spectrum, especially for the region above 7.7 eV [5]. The vibrational pattern of the photoelectron spectrum ($\tilde{X}^2A_2 \leftarrow \tilde{X}^1A_1$ transition) and ab initio calculations have been used by Palmer et al. [5] for the analysis–interpretation of the absorption spectrum measured by synchrotron light. The photoelectron spectrum shows a well-resolved vibrational structure for the lowest ionic state (\tilde{X}^2A_2) and the assignment of this structure was attempted by Derrick et al. [4,6]. Derrick et al. [6] compared the vibrational structure of the \tilde{X}^2A_2 ionic state for four related molecules, furan, thiophene, pyrrole and cyclopentadiene. From this comparison and by taking into account the frequencies in the ground state, the vibrational pattern of the photoelectron band was assigned (three

active a_1 modes, ν_8 , ν_6 and ν_3). In the present work, the numbering of the modes follows the Mulliken scheme [7]. The pictures of the normal mode coordinates of vibrations can be seen in refs. [7,8]. The IR/Raman spectra of furan and its deuterated derivatives have also been studied by Rico et al. [9].

The application of the resonance-enhanced multiphoton ionization (REMPI) technique, has contributed in the understanding of furan's electronic transitions. Cooper et al. [10] gave new results and assignments for the Rydberg states of furan by measuring the room temperature (2 + 1), (3 + 1) and (4 + 1) REMPI spectra with laser light $\lambda > 360\text{ nm}$. A clear interpretation of the Rydberg states of furan has been given recently [11]. Ridley et al. [11] measured the (2 + 1) and the (3 + 1) REMPI spectra of jet-cooled C_4H_4O and C_4D_4O in the $50,800\text{--}72,000\text{ cm}^{-1}$ spectroscopic region. In two- and three-photon spectroscopy, all the transitions are allowed (in one-photon, the $A_1 \rightarrow A_2$ are forbidden). Moreover, linearly and circularly polarized light was used in order to successfully clarify the symmetry of the excited states. The ionization energy (I.E.) of furan is $71,673\text{ cm}^{-1}$ [11,12]. Regarding the one-photon forbidden $1a_2 \rightarrow 3s(^1A_2)$ Rydberg state [13], Roebber et al. [14] have detected a band at $47,700\text{ cm}^{-1}$, in the room temperature multiphoton ionization spectrum of furan (λ laser $\sim 419\text{ nm}$), and interpreted this feature as the $1a_2(A_1) \rightarrow 3s(^1A_2)$ transition. This interpretation seems to be complicated by the three-photon ionization threshold ($3h\nu = 71,550\text{ cm}^{-1}$) which is very close to the I.E. value. However, the high-resolution electron energy loss spectrum [15] shows the presence of a transition at $\sim 47,700\text{ cm}^{-1}$.

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In all molecules, the vibrational fine structure is of fundamental importance in both electronic and photoelectron spectroscopy [16]. Furan is non-fluorescing and therefore, dispersed fluorescence spectra are not viable. In the present work, we employ a direct method to find the active vibrations by detecting the hot bands, which may appear in an electronic transition. Inspection of the REMPI spectra [11] shows that the (2 + 1) REMPI signal of the $1a_2 \rightarrow 3d_{xy}(^1A_1)$ Rydberg transition is very strong and there is no other transition, 2000 cm^{-1} further to the red side of this origin. Therefore, the hot bands can be detected by studying the REMPI spectra under cold and warm-beam conditions. The laser light was tuned in the 350–310 nm and 688–648 nm regions to elucidate the vibrational activity in the two- and four-photon induced transitions (spectroscopic region $57,100\text{--}64,500\text{ cm}^{-1}$). A complete vibronic analysis of the observed 3d states is given. The understanding of the electronic transitions of furan is a prerequisite for the interpretation of the electronic transitions of 2-methylfuran. The absorption and photoelectron spectra of 2-methylfuran have been studied recently [17] and in our laboratory we are studying this molecule by the REMPI technique [18].

2. Experimental

Furan, seeded in Ar, was expanded into a vacuum chamber through a pulsed valve of 0.50 mm orifice diameter (General Valve Corporation, Iota One). The Ar pressure could be regulated in the 1–3 atm range. In order to ensure an oil free chamber, a liquid nitrogen trap was used. The supersonic molecular beam was crossed by the laser beam at about 4 cm from the valve orifice. The laser light was focused in the molecular beam by a $f = +15\text{ cm}$ lens. A pulse generator (SRS, model DG535) synchronized the laser pulse to the pulsing valve. By adjusting the delay between valve opening and laser firing, cold or warmer molecules could be selected. Also, the duration of the valve activation had an influence on the cooling conditions. The $\sim 4\text{ ns}$ laser light was produced by a Nd:YAG pumped dye laser (Lambda Physik, Scanmate 2EC-400). The wavelength region 700–620 nm ($\sim 5\text{ mJ/pulse}$) was produced using the LC7100 dye, the LC6500 dye and the LC6400 dye. A mixture of the first two dyes was also used in some experiments in order to have an approximate constant dye profile in the whole wavelength region. For the production of the UV laser light (350–310 nm), a BBO III SHG crystal was installed (power of the UV laser $\sim 1\text{ mJ/pulse}$). The produced ions were analyzed in a TOF mass spectrometer (Wiley–McLaren type, 1 m long, R.M. Jordan Co.). The TOF mass spectra were measured on a LeCroy 9310C digital oscilloscope. The UV wavelength-tuned spectra ((2 + 1) REMPI) were recorded by gating the parent ion (Stanford Research SR250 boxcar integrator). The experiments were repeated by gating the fragment C_3H_3^+ and some lighter mass ions. The (4 + 1) REMPI spectra (red light) were recorded by gating the fragment C_3H_3^+ . In the experiments with the red light, the parent ion was absent.

The spectra have been calibrated by the two-photon transitions $2p^2\ ^1D_2 \rightarrow 2p3p\ ^1D_2$ ($\lambda_{\text{laser}} = 320.327\text{ nm}$) and $2p^2\ ^1D_2 \rightarrow 2p3p\ ^1S_0$ ($\lambda_{\text{laser}} = 313.471\text{ nm}$) of the carbon atom

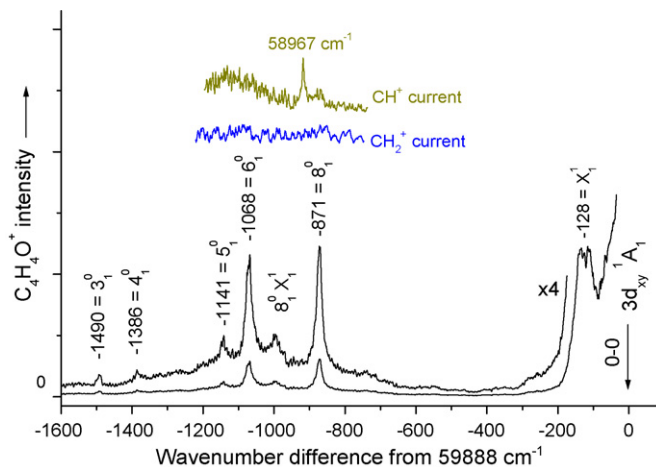


Fig. 1. The (2 + 1) REMPI spectrum of jet-cooled furan, under “warm” molecular beam conditions. The tuning range of the laser wavelength is 343.1–334 nm (hot bands of 3d A_1 Rydberg state). The origin is out of scale. The spectrum on the top is recorded by gating the CH^+ fragment (see discussion at the end of the paper).

(neutral C is produced from the laser multiphoton decomposition of furan) and by the very sharp three-photon argon lines $3p^6\ ^1S_0 \rightarrow 3p^5\ 4s[3/2]_1$ ($\lambda_{\text{laser}} = 319.905\text{ nm}$) and $3p^6\ ^1S_0 \rightarrow 3p^5\ 4s[1/2]_1$ ($\lambda_{\text{laser}} = 314.375\text{ nm}$).

3. Results and discussion

The REMPI measured spectra of furan are presented in Figs. 1–3. Fig. 1 shows the hot band region of the $1a_2 \rightarrow 3d_{xy}(^1A_1)$ transition. In Fig. 2, the cold bands of the $1a_2 \rightarrow 3d_{xy}(^1A_1)$ and $1a_2 \rightarrow 3d(^1A_2)$ transitions have been displayed. The progressions (combination bands to the 3d A_1) are demonstrated in Fig. 3.

The spectrum of Fig. 1 was recorded under “warm” molecular beam conditions. The (2 + 1) REMPI origin band is very

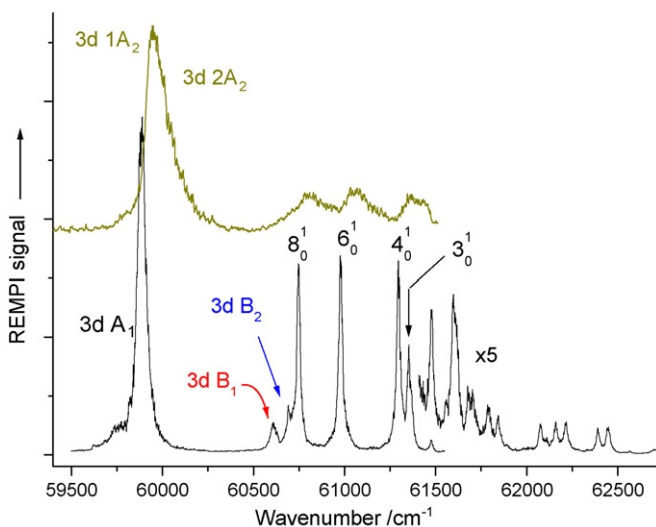


Fig. 2. The (2 + 1) REMPI (signal of the parent ion $\text{C}_4\text{H}_4\text{O}^+$) and the (4 + 1) REMPI (signal of the fragment ion C_3H_3^+) spectra of jet-cooled furan. The (4 + 1) REMPI spectrum is at the top (vertically up-shifted). The sensitivity of the vertical scale is not the same for the two spectra.

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