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A study of the excited electronic states of normal and fully deuterated furan by photoabsorption spectroscopy and high-level ab initio calculations

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ABSTRACT

The photoabsorption spectra of C_4H_4O and C_4D_4O have been measured between ~5.5 and 17.7 eV using a synchrotron radiation-based Fourier transform spectrometer. In addition to several broad bands due to transitions into valence states, the spectra exhibit numerous sharp bands associated with Rydberg states belonging to series converging onto the $\tilde{X}\,^2A_2$ or the $\tilde{A}\,^2B_1$ state limits. Vertical excitation energies and oscillator strengths have been computed using the second- and third-order algebraic-diagrammic construction polarisation propagator methods (ADC(2) and ADC(3)), and the equation-of-motion coupled-cluster method at the level of singles and doubles model (EOM-CCSD). Adiabatic excitation energies have been estimated using previously computed corrections. The theoretical predictions have allowed assignments to be proposed for the Rydberg series observed in the present single-photon absorption spectra and for some additional series, mainly of A_2 symmetry, reported in previous multiphoton excitation studies. The assignments of some of the Rydberg series converging onto the $\tilde{A}\,^2B_1$ state limit have been revised and, guided by our calculations, the principal series is ascribed to the $2b_1 \rightarrow nda_2\ ^1B_2$ and $2b_1 \rightarrow ndb_1\ ^1A_1$ transitions. f-type Rydberg series, previously observed only in the multiphoton absorption spectrum of furan, have been observed and assigned. Such f-type series, converging onto either the $\tilde{X}^2A_2$ or the $\tilde{A}\,^2B_1$ state thresholds, contribute significantly to the single-photon absorption spectrum. Many of the absorption bands associated with Rydberg states display vibrational progressions which resemble those in the corresponding photoelectron band. It appears that some of the structure associated with the $1a_2 \rightarrow 3pb_2\ ^1B_1$ and $1a_2 \rightarrow 3pb_1\ ^1B_2$ transitions involves excitation of non-totally symmetric vibrational modes.

1. Introduction

The first few excited states of furan (Fig. 1) have attracted considerable attention due to their unusual and complex spectroscopic and dynamical properties. Extensive theoretical investigations have shown that the potential energy surfaces corresponding to the two lowest Rydberg states and to the two lowest valence excited states are vibronically coupled, and that the associated conical intersections affect both the photoabsorption spectrum [1–3] and the photochemical transformations [4–8]. The UV single-photon absorption spectrum of furan is well established [9–16], and is dominated by two very broad and intense bands, associated with valence states, centred at ~6 and 8 eV. Weak and irregular vibrational structure appears in the near-threshold region of the lower of these bands, and some much sharper and stronger peaks, due to Rydberg states belonging to series converging onto the ground ($\tilde{X}\,^2A_2$) state ionisation limit, have long been known in the higher energy region. However, a consistent set of assignments for the Rydberg structure has yet to be achieved.

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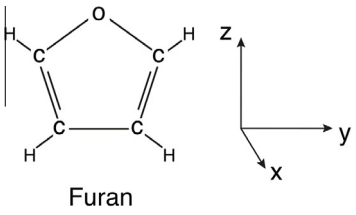

Fig. 1. Schematic representation of furan showing the axis orientation.

Recent progress towards an improved understanding of the Rydberg series converging onto the $\tilde{X}\,^2A_2$ state limit has been made in the mass-resolved (2 + 1) and (3 + 1) resonance enhanced multiphoton ionisation (REMPI) experiments on jet cooled C_4H_4O and C_4D_4O performed by Ridley et al. [17,18]. By taking advantage of the propensity rules which govern the relative intensities of two- or three-photon transitions, and by studying the polarisation dependence of the signal when using linearly or circularly polarised light, Ridley et al. were able to identify several d-type and f-type Rydberg series. Moreover, as the selection rules for two- or three-photon transitions differ from those for one-photon transitions, excited states of A_2 symmetry, which are forbidden in single-photon absorption from an initial state of A_1 symmetry, could be accessed. These studies were, nevertheless, hampered by the lack of theoretical predictions to guide the Rydberg state assignments.

An interesting point to emerge from the REMPI experiments [17,18] was the observation of structure attributed to *n*f Rydberg series. f-type Rydberg states have also been identified in recent high resolution photoabsorption studies of propyne [19] and 1-butyne [20], and their appearance has been discussed in relation to the character of the highest occupied molecular orbital (HOMO). In small molecules, the transition moment between the HOMO, which tends to be penetrating, and a Rydberg orbital of high orbital angular momentum (l), which tends to be non-penetrating, is small. However, in larger molecules the transition probability to such states may increase because the more extended nature of the molecular frame results in some of the high-l states having a penetrating character. The HOMOs in propyne and 1-butyne are similar [19–22], with both containing substantial atomic *n*p and *n*d character. As the single-photon selection rule for atomic transitions suggests that the oscillator strength for $l \rightarrow l+1$ transitions should be substantially higher than that for $l \rightarrow l-1$ transitions [23], the d-component of the HOMO should favour excitation into f-type Rydberg states. The HOMO in furan [22] has a nodal structure which resembles a distorted dπ orbital. Thus, in a simple, highly qualitative picture, the appearance of f-type Rydberg states in furan might not be unexpected.

In the present work, high resolution photoabsorption spectra of C_4H_4O and C_4D_4O have been recorded with the Fourier transform spectrometer (FTS) [24] at the Soleil synchrotron radiation facility. The photon energy range (5.5–17.7 eV) has allowed Rydberg series converging onto the $\tilde{X}\,^2A_2$, $\tilde{A}\,^2B_1$ or $\tilde{G}\,^2A_1$ state ionisation thresholds to be studied. The assignments of the observed structure are based on transition energies and oscillator strengths calculated in our complementary theoretical investigations.

The electronic excitation spectrum of furan has been the subject of many previous theoretical studies [15,25–33], the most relevant of which are those of Pastore et al. [32] using multireference perturbation theory (NEVPT), Wan et al. [30] employing the symmetry-adapted cluster configuration-interaction (SAC-CI) method, and Christiansen and Jørgensen [29] who performed linear response (LR) coupled cluster (CC) calculations using the CCSD and CC3 models. In this latter work, adiabatic transition energies were evaluated using excited-state geometry optimisation at the level of the CC2 model. Adiabatic energy corrections for many of the singlet excited states were also obtained in our previous ADC(2) study [28] where, for the first time, an attempt was made to interpret the experimental photoabsorption spectrum at a level beyond the vertical excitation picture.

To facilitate the assignment of the structure observed in the present photoabsorption spectrum, transition energies and oscillator strengths of the vertical excitations have been computed using the ADC(3) [34–36], ADC(2) [37–41] and (EOM-CCSD) [42–45] approaches. An extended basis set, which included f-type Rydberg functions, has been employed in these calculations, thereby allowing many of the Rydberg states to be reproduced. The inclusion of f-type Rydberg functions proved to be an important step because some of the most intense bands in the experimental spectrum are due to such excitations. Adiabatic excitation energies have been estimated using corrections computed at the ADC(2) level in earlier work [28]. Since the CCSD results are generally only slightly less accurate than the ADC(3) results [34,35], we use both sets of data to check the consistency of our predictions. For the same reason, we compare our results with those of Christiansen and Jørgensen [29], which are the best, already available, theoretical estimates.

2. Experimental apparatus and procedure

The photoabsorption spectra of C_4H_4O and C_4D_4O were recorded using the FTS [24] attached to the DESIRS beamline [46] at the Soleil synchrotron radiation source. Detailed descriptions of the beamline, spectrometer and experimental procedure have been reported in our previous work on thiophene [47] so only a brief account is given here.

The undulator-based beamline provides radiation covering the energy range ~5–40 eV, and a portion of this distribution, with a bandwidth of ~7% of the central energy, can be selected by tuning the undulator. This radiation passes through a cell containing the gaseous sample before entering the FTS. Two types of cell were used in the present work. The first was windowless and, by employing long entrance and exit capillaries, maintained a quasi-static column of gas, thereby allowing a relative absorption spectrum to be measured across the entire photon energy range. The second cell used MgF_2 entrance and exit windows, and was used to determine the absolute photoabsorption cross section over a limited energy range. The latter spectrum was used to calibrate the full VUV spectrum obtained with the windowless cell, with the resulting experimental uncertainty being about ±10%. This estimation represents an upper limit of the potential error at the high photon energy end of the spectrum. It is difficult to provide a more precise evaluation due to the complicated nature of assembling a composite spectrum from the individual sections. A detailed discussion of this process, together with a consideration of the energy dependent sources of error, will be given in a forthcoming publication [48].

The photon energy scale, which is intrinsically linear, was calibrated by using the absorption line due to the Ar $3p^6\ ^1S_0 \rightarrow 3p^5(^2P_{1/2})4s$ transition at 11.8282 eV [49]. A small peak due to this state appears in the absorption spectrum and originates from the gas filter used to attenuate the high harmonics.

The composite photoabsorption spectra of C_4H_4O and C_4D_4O, plotted in Fig. 2, have been assembled by combining those measured in the individual, overlapping spectral windows (undulator settings). The spectra shown were recorded with resolutions of 0.86 and 1.07 meV (FWHM) for C_4H_4O and C_4D_4O, respectively. Spectra measured with a resolution of 0.43 meV revealed no additional features. Thus, the line widths of the absorption bands are not resolution limited. The absolute photoabsorption cross