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Pure Rotational Spectrum of Dibenzofuran in Range of 2–6 GHz[†]Hai-hua Zhou^a, Zeng-kui Liu^a, Zi-qiu Chen^{a*}, Ming Sun^{b*}, Qian Chen^{b*}, Sheng-wen Duan^b, Chao Jiao^b*a. College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, China**b. School of Electronic and Optical Engineering, Nanjing University of Science and Technology, Nanjing 210094, China*

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We report the observation and assignment of the rotational spectra of dibenzofuran measured in the range of 2–6 GHz with a newly constructed broadband chirped-pulse Fourier transform microwave (cp-FTMW) spectrometer. An analysis of the microwave spectra led to the assignment of 40 *b*-type transitions, resulting in the accurate determination of the rotational constants $A=2278.19770(38)$ MHz, $B=601.12248(10)$ MHz, and $C=475.753120(98)$ MHz.

Key words: Dibenzofuran, Polycyclic aromatic hydrocarbons, Broadband rotational spectroscopy

I. INTRODUCTION

The origin of ubiquitous unidentified infrared emission (UIR) features seen in the interstellar medium (ISM) remains a mystery. Although polycyclic aromatic hydrocarbons (PAHs) are widely believed to be the carriers for the UIR bands [1, 2], the molecular specific identification has been proven difficult using the commonly employed rotational spectroscopy in radio astronomy due to the often small or zero dipole moment that many PAHs possess. On the other hand, the search for simple aromatic molecules that are likely linked to the formation of PAHs but easier to observe, seems to be a valid approach to constrain models in interstellar chemistry. Dibenzofuran has been proposed to lead to PAH formation at temperatures above 800 °C through oxidation pathways [3]. In this context, as a simple oxygenated PAH with considerable dipole moment, it would serve as a candidate for the detection of PAHs in the ISM.

Dibenzofurans have been observed in ambient air [4] and its formation can be attributed to the same source as unsubstituted PAHs such as incomplete combustion in waste incineration [5, 6]. As an oxygenated PAH, dibenzofurans are produced through secondary oxidation of PAHs by chemical and microbiological processes [7, 8]. Higher toxicity such as mutagenicity and carcinogenicity has been shown over the parent PAHs in oxygenated PAHs [9]. Dibenzofuran in particular, undergoes oxidation reactions with OH radicals, NO₃ radicals and O₃ in the atmosphere [10], making the information pertaining to its gas-phase structure and spectroscopy

of fundamental interest. Dibenzofuran can serve as a prototype of this class of substituted PAHs to be studied by spectroscopy as this tricyclic moiety is present in this family of compounds.

Up to date, dibenzofuran has been investigated by vibrational spectroscopy [11, 12] and rotationally-resolved electronic spectroscopy [13–15]. This work aims to extend the range of laboratory spectroscopy to support the astrophysical observation of potential precursor molecules for multi-ring PAHs through a microwave investigation of its pure rotational spectrum. We report the measurement and analysis of the observed spectra of dibenzofuran in the vibrational ground state in the range of 2–6 GHz.

II. METHODS

A. Experiments

The rotational spectra of dibenzofuran were recorded using a chirp-pulse Fourier Transform microwave (cp-FTMW) spectrometer working between 1 and 18 GHz recently developed at Nanjing University of Science and Technology (NJUST) described in detail [16, 17]. In short, a chirped pulse is produced by mixing linear frequency sweeps generated by an arbitrary wave form generator (Tabor WX1281, 1.25 GS/s, 1 GHz) and the cw output of a microwave synthesizer (Anapico Ap-syn420, 1–18 GHz). This broadband pulse is then amplified using a solid state amplifier (BONN, 5W) before being coupled to the custom-built vacuum chamber which contains a pair of high gain horn antenna for broadcasting and receiving the microwave signal. The vacuum chamber is pumped through a molecular pump with a background pressure around 1×10^{-5} Pa. A gas mixture of noble gas seeded with sample molecules was allowed to enter the vacuum chamber through a pulsed solenoid valve with a diameter of 1.0 mm (Parker Se-

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ries 9). The pulsed valve was designed to heat up to 250 °C to obtain sufficient vapor pressure for certain solid chemicals.

The molecular emission is first amplified by a low-noise amplifier (Miteq AFS44 LNA, 1–18 GHz) before being down converted using the microwave synthesizer, which is subsequently digitized using a 2.5 GHz bandwidth oscilloscope (Lecroy WaveRunner 6 Z). Fast Fourier transformation of the resulting free induction decay leads to the broadband spectrum over the full bandwidth of the chirp. The whole sequence can be repeated to produce multiple free induction decays (FIDs) so that the resulting spectrum gives improved signal-to-noise ratio. The microwave synthesizer, the arbitrary wave form generator and the oscilloscope are referenced to a 10 MHz rubidium standard (Stanford Research Systems, FS725) for external stability.

As dibenzofuran is a non-volatile molecule with a vapour pressure of ca. 27 Pa at room temperature, a simple heating unit was included within the pulsed nozzle assembly to increase the temperature to 200 °C at which a vapour pressure higher than 120 Pa is expected. A pressure of 0.6 MPa argon was then allowed to pass over the sample as carrier gas for the supersonic jet expansion.

The excitation frequency from the microwave synthesizer was mixed with a 5 μ s linear frequency sweep, or “chirp”, from 0 to 500 MHz, leading to a 1 GHz bandwidth of excitation. The resultant free induction decay (FID) was collected at a sampling rate of 40 GSa/s for 40 μ s, giving a spectral resolution (full-width-at-half-maximum) of 80 kHz. The data acquisition sequence was repeated and a total of 1,000,000 FIDs were averaged to produce the spectrum via fast Fourier transformation. A total of four 1 GHz scans were used to cover the 2–6 GHz region. An overview spectrum of one such 1-GHz window is presented in FIG. 1 with a section showing assigned transitions in FIG. 2.

B. Computation

Both *ab initio* and density functional theory (DFT) methods were employed to optimise the ground state structure of dibenzofuran. The *ab initio* calculation was carried out using the second order Møller-Plesset perturbation theory (MP2) [18] while the DFT calculation was performed using the Becke, 3-parameter, Lee-Yang-Parr (B3LYP) [19, 20], exchange-correlation functional with the correlation consistent polarised valence n-tuple ζ (cc-pVnZ, $n=D$ and T here) basis sets. The augmentation of such basis sets was not used as Treitel and co-workers concluded that the inclusion of diffuse functions does not improve the calculated geometrical parameters for PAH anions significantly [21]. All geometric optimisations were carried out using the Gaussian 09 package [22], and the calculated rotational constants and dipole moment are shown in Table I. The Cartesian coordinates of the optimised structures calculated

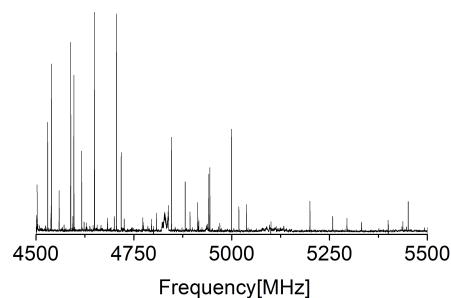


FIG. 1 An overview of the microwave spectrum of dibenzofuran between 4.5 and 5.5 GHz measured with 1,000,000 FIDs.

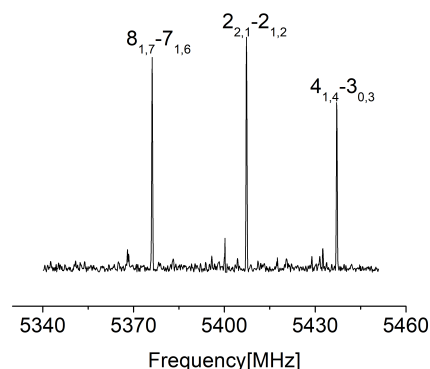


FIG. 2 A zoomed-in spectrum of the microwave spectrum of dibenzofuran with three assigned transitions.

using each level of theory and basis set can be found in supplementary materials.

III. ASSIGNMENT AND RESULTS

A. Effective Hamiltonian

The analyses of the pure rotational spectra in the GHz and THz regions were carried out using Watson’s *A*-reduced effective Hamiltonian [23] in the I^r representation, which is shown here including up to sextic centrifugal distortion constants:

$$\begin{aligned} \hat{H}_{\text{rot}}^{v,v} = & A_v \hat{J}_z^2 + B_v \hat{J}_x^2 + C_v \hat{J}_y^2 - \Delta_v^J \hat{J}^4 - \Delta_{JK}^v \hat{J}^2 \hat{J}_z^2 + \\ & \Delta_K^v \hat{J}_z^4 - \frac{1}{2} \left[\left(\delta_v^J \hat{J}^2 + \delta_v^K \hat{J}_z^2 \right), \left(\hat{J}_+^2 + \hat{J}_-^2 \right) \right]_+ + \\ & \phi_J^v \hat{J}^6 + \phi_{JK}^v \hat{J}^4 \hat{J}_z^2 + \phi_K^v \hat{J}^2 \hat{J}_z^4 + \phi_K^v \hat{J}_z^6 + \\ & \frac{1}{2} \left[\left(\eta_v^J \hat{J}^4 + \eta_{JK}^v \hat{J}^2 \hat{J}_z^2 + \eta_K^v \hat{J}_z^4 \right), \left(\hat{J}_+^2 + \hat{J}_-^2 \right) \right]_+ \end{aligned} \quad (1)$$

where with $i = \sqrt{-1}$, we have the angular momentum operators:

$$\hat{J}^2 = \hat{J}_x^2 + \hat{J}_y^2 + \hat{J}_z^2, \quad \hat{J}_{\pm} = \hat{J}_x \pm i \hat{J}_y$$

All observed transitions were fitted using the I^r representation in the Pickett’s SPFIT/SPCAT spectral fitting programme [24].

TABLE I Computational results for dibenzofuran ($\Delta^a=0$).

	MP2				B3LYP			
	A/MHz	B/MHz	C/MHz	μ_b /Debye	A/MHz	B/MHz	C/MHz	μ_b /Debye
cc-PVDZ	2246.5932	594.1975	469.9115	0.95	2272.2345	596.8886	472.7127	0.61
cc-PVTZ	2283.6884	603.4914	477.3469	0.89	2297.1707	602.6643	477.4143	0.66

$$^a \Delta = I_c - I_a - I_b$$

B. Assignment of the pure rotational spectra in the ground state

Dibenzofuran is an asymmetric rotor of C_{2v} symmetry. Its permanent electric dipole moment is expected to lie along the b -axis allowing transitions to obey b -type selection rules ($eo \leftrightarrow oe$ and $oe \leftrightarrow eo$, e for even and o for odd values of the quantum numbers K_a and K_c) [25]. The principal axis system for dibenzofuran is given in FIG. 3.

The assignment of the observed spectra in the range of 2–6 GHz was assisted by a simulation of the spectrum using the calculated rotational constants at MP2/cc-pVTZ level. A total of 40 b -type transitions were assigned using the PGOPHER programme [26, 27] in the range of 2–6 GHz with $J_{\max}=19$ and $K_{a \max}=5$. The assigned transitions were fitted and the resulting spectroscopic parameters are given in Table II. The root-mean-square deviation d_{rms} of the fit is 4 kHz, with the typical linewidths (full-width at half-maximum) of about 80 kHz. A full list of the assigned transitions is provided in supplementary materials.

IV. DISCUSSION

Pure rotational transitions were measured and assigned from 2 GHz to 6 GHz, providing the first study in the microwave range. This allowed for an accurate determination of the rotational constants. Comparing the rotational constants with values obtained from reported high resolution electronic spectroscopy studies [14, 15], the accuracy of our values is improved by at least two orders of magnitude as shown in Table II, reflecting the high resolution of Fourier transform microwave (FTMW) over techniques in the optical range. The root-mean-square deviations (σ_{rms}) of the fit of 4.6 kHz is considerably less than one-tenth of the ~ 80 kHz observed linewidths, suggesting the effective Hamiltonian employed here provides an accurate description of observed spectral features in this range. As a result, the spectroscopic parameters reproduce the experimental spectrum very well. In comparison, the σ_{rms} values in Ref.[14] and Ref.[15] are a few MHz. It is worth mentioning that such an agreement was achieved by including only three rotational constants in the fit while centrifugal distortion constants were found not sensitive to the observed transitions in this study.

All calculations in this study show a planar structure for dibenzofuran with C_{2v} symmetry, indicating

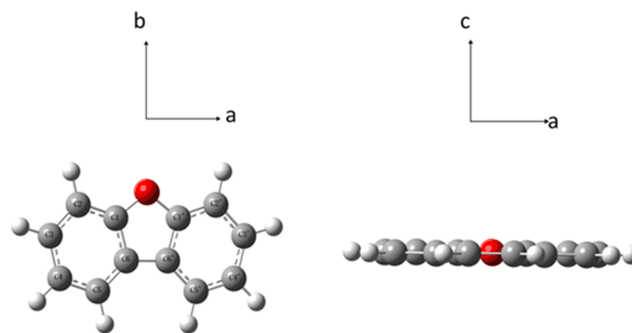


FIG. 3 Structure of dibenzofuran (carbon atoms are labeled in grey and oxygen in red). The C_2 symmetry axis coincides with the b -axis. Axes definition in the principal inertial axis system is shown at the top. The c -axis is perpendicular to the ab plane.

the only non-zero dipole moment being along the C_2 axis which coincides with the b -axis through the oxygen atom as shown in FIG. 3. This is consistent with the experimental findings that only b -type transitions were observed. Although the experimentally obtained rotational constants alone were not enough for accurate structural determination, one can determine the inertial defect to verify the expected planar cyclic structure. Dibenzofuran with a C_{2v} is expected to have a zero inertial defect as it is planar (see Table II). However, our value of the inertial defect calculated using the experimental rotational constants is -0.285652 . As it is a slightly negative number, we can attribute it to the averaging of vibrational levels of the out-of-plane, low-lying, large amplitude motions that are often associated with PAHs. In particular, the “butterfly” motions are ubiquitous in tricyclic molecules and the fundamental of such motion in dibenzofuran is at only $\sim 100 \text{ cm}^{-1}$ [28].

V. CONCLUSION

In the current study, we presented the first spectroscopic study of dibenzofuran in the microwave region. It has been demonstrated that cp-FTMW is capable of measuring such a non-volatile molecule in a supersonic jet. The results from this work have the potential to guide the astrophysical and atmospheric searches for this molecule via remote sensing. It has been observed that the equilibrium structure of this tricyclic

TABLE II Spectroscopic constants for the ground state of dibenzofuran.

	A/MHz	B/MHz	C/MHz	N	σ/kHz	$\Delta/(\text{amu}\cdot\text{\AA}^2)$
MW	2278.19770(38)	601.12248(10)	475.753120(98)	40	4.616	-0.285652
Ref.[14]	2278.104(23)	601.003(33)	475.675(30)	3138	14333	-0.288523
Ref.[15]	2278.2(1)	601.1(1)	475.8(1)		2140	

Note: values in parenthesis provide statistical 1σ uncertainties in units of the last specified digits.

molecule has coupled with the low-lying, out-of-plane modes and our accurately determined rotational constants can provide the basis for the rovibrational studies of such modes in the far-infrared region.

Supplementary materials: The line list of assigned transitions as well as the theoretical geometric parameters of dibenzofuran is included in the electronic supplementary data.

VI. ACKNOWLEDGMENTS

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