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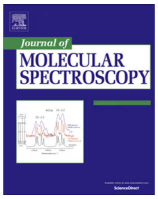

Microwave spectrum and the gas phase structure of phthalimide

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ABSTRACT

The microwave spectrum of phthalimide (PhI) was measured in the 4.8–9.5 GHz range using a Flygare-Balle type, pulsed-beam Fourier transform microwave spectrometer. Rotational transitions were measured for the parent and all unique single ^{13}C substituted isotopologues. The rotational (MHz), centrifugal distortion (kHz), and quadrupole coupling constants (MHz) were determined for the parent to be $A = 1745.6655(10)$, $B = 1199.3309(6)$, $C = 711.0864(3)$, $D_J = 0.012(7)$, $D_{JK} = -0.05(9)$, $1.5\chi_{aa} = 2.719(11)$, and $0.25(\chi_{bb} - \chi_{cc}) = 1.236(3)$. Using the measured rotational constants of the isotopologues, a nonlinear least squares fit was performed to obtain the best fit gas phase structure. The inertial defect is $\Delta = -0.175$ amu Å^2, indicating a planar structure for PhI.

Calculations using B3LYP/aug-cc-pVQZ provided rotational constants which are much closer to the experimental values compared to the MP2/6-311++G** calculated values.

1. Introduction

Phthalimide (PhI) and its derivatives are important compounds, widely utilized in industry as well as in medicinal chemistry due to the biological activity of PhI and its derivatives. Synthesized derivatives of PhI used in medicinal chemistry have been found to have a wide range of biological activities, including antitumor, anti-inflammatory, and antimicrobial properties [1]. PhI derivatives are also used to interact with liver receptors that are involved in the regulation of cholesterol, lipid and glucose metabolism [2]. In industry, PhI is used in plastics, plasticizers, and is also used in the synthesis of peptides and as a masked source for amines [3].

Phthalimide, $C_6H_4(CO)_2NH$, or isoindole-1,3-dione (IUPAC) has a melting point of 237–238 °C [4]. PhI is a solid white crystal and can be obtained by heating phthalic anhydride with ammonia or another amine source, such as ammonium carbonate or ammonium acetate [5]. The vapor pressure of PhI at 90 °C is ~0.01 Torr [6], sufficient to measure the rotational transitions using pulsed-beam Fourier transform (PBFT) microwave spectroscopy. The crystal structure of PhI was initially determined by Matzat [7] using data collected from the mineral kladnoite. The IR spectrum was measured by Binev et al. [8] and they also obtained structural parameters. In order to further refine the structure, Glidewell et al. performed an X-ray crystallography analysis on PhI that was crystallized with pyridine [9]. However, the X-ray structures are modified by packing effects and distortions, so it is also important to measure the pure rotational spectrum of PhI in an attempt obtain an accurate gas phase structure.

2. Microwave measurements

The phthalimide sample was purchased from Sigma Aldrich (99%) and was used without further purification. A pulsed-beam Fourier transform microwave spectrometer, described previously [10,11], was used to make microwave measurements in the 4.8–9.5 GHz range for the parent isotopologue and these transitions are shown in Table 1. Ne was used as the carrier gas and the backing pressure was set to ~1 atm. Prior to the pulsed injection of the molecular sample, the pressure inside the microwave cavity was maintained at 10^{-6} to 10^{-7} Torr and the pulsed valve was heated to ~125–130 °C in order to obtain sufficient vapor pressure of the sample to obtain a parent test signal in one pulsed-beam cycle. The unique ^{13}C isotopologues of PhI were measured in the same way as the parent in the 4.8–6.5 GHz range. The labeling scheme used to describe the isotopic substitutions is shown in Fig. 1 and the measured rotational transitions for all the ^{13}C isotopologues are shown in Table 2.

3. Calculations

Ab initio calculations were performed using the Gaussian-09 suite [12] on the high performance computing system at the University of Arizona to obtain an optimized structure and predict the rotational transitions. Calculations were performed using MP2

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Table 1
Measured rotational transitions (ν_{obs}) of the parent isotopologue shown in MHz and deviations of the best fit calculated frequencies from the observed values ($\nu_{o\text{-}c}$).

J' Ka′ Kc′ F'	J'' Ka″ Kc″ F''	ν_{obs}	$\nu_{o\text{-}c}$
3134	2123	4885.647	−0.001
3132	2121	4885.773	0.002
3133	2122	4885.932	−0.004
3133	2123	4887.012	−0.002
3032	2022	5057.851	−0.004
3034	2023	5059.259	−0.002
3032	2021	5059.336	0.008
3033	2022	5059.637	0.010
3033	2023	5060.568	−0.005
4234	4044	5076.449	−0.003
4235	4045	5077.656	−0.005
4233	4043	5077.972	0.000
3222	2211	5730.793	−0.006
3224	2213	5731.123	0.000
3223	2213	5731.123	0.000
3223	2212	5731.703	−0.002
3222	2212	5731.703	−0.002
3122	2111	6285.845	−0.002
3124	2113	6286.060	0.000
3123	2112	6286.374	0.002
4145	3134	6368.981	−0.005
4143	3132	6369.065	0.002
4144	3133	6369.185	0.003
3212	2201	6402.812	−0.000
3214	2203	6403.096	0.005
3213	2202	6403.328	−0.002
4045	3034	6437.139	−0.004
4043	3032	6437.206	0.003
4044	3033	6437.383	−0.002
2201	1011	7194.918	0.001
2203	1012	7194.940	0.005
4233	3222	7468.723	0.008
4233	3223	7468.723	0.008
4235	3224	7468.799	−0.005
4234	3223	7469.146	−0.003
4234	3224	7469.146	−0.003
5156	4145	7813.517	−0.002
5154	4143	7813.568	−0.005
5155	4144	7813.672	0.009
5056	4045	7834.351	0.000
5054	4043	7834.396	−0.005
5055	4044	7834.499	−0.010
4133	3122	7993.887	0.005
4133	3124	7993.953	0.003
4135	3124	7993.988	−0.005
4134	3123	7994.350	−0.004
5244	4233	9088.837	0.009
5246	4235	9088.871	0.007
5245	4234	9089.131	−0.000
6167	5156	9242.336	−0.000
6165	5154	9242.377	−0.001
6166	5155	9242.445	−0.000
6067	5056	9247.940	0.003
6065	5054	9247.975	−0.003
6066	5055	9248.051	0.002

[13] and DFT (B3LYP) methods with 6-311++G** and aug-cc-pVQZ basis sets respectively. The calculated rotational and quadrupole coupling constants from each calculation were used in Pickett's SPCAT [14] program to predict the rotational transitions of the parent isotopologue.

In order to predict the rotational constants of all the unique ^{13}C isotopologues, first the ratios between the experimentally determined parent rotational constants and the MP2/6-311++G** calculated rotational constants were determined. After changing the mass of the ^{13}C atom within the calculated molecular structure and recalculating the rotational constants of the new structure, these rotational constants for each isotopologue were multiplied by the previously determined experimental/calculated ratio to obtain corrected rotational constants of the ^{13}C isotopologues. These corrected values were within <1% of the final experimentally fit values. These corrected rotational constants and the quadrupole coupling constants of the parent were used in the SPCAT program to predict the ^{13}C isotopologue rotational transitions.

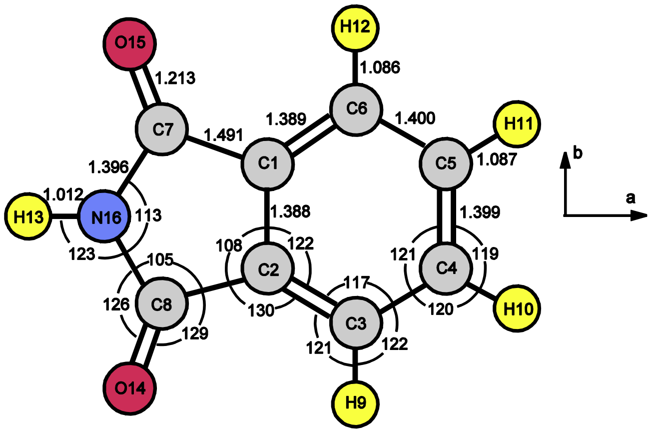

Fig. 1. The structure of phthalimide obtained by fitting the measured rotational constants for all measured isotopologues. The top section shows bond lengths (top, in Å) and bottom shows interbond angles (bottom, in °). Also shown are the directions of the *a* and *b* principle axes for the molecule.

4. Rotational constants

The rotational constants for the parent and all unique ^{13}C isotopologues were determined using Pickett's SPFIT [14] program and these results are shown in Table 3. While fitting the measured rotational transitions of the unique ^{13}C isotopologues, the centrifugal distortion constants (D_J and D_{JK}) were held fixed to values obtained from the fit for the parent. The rotational constants obtained from the best fit gas phase structure are shown with the experimentally fit rotational constants of all the isotopologues and the measured–calculated differences (M − C) of these values are listed in Table 4. Differences between the calculated rotational constants of the best fit structure and its isotopologues had a standard deviation of 0.14 MHz. The B3LYP/aug-cc-pVQZ calculated rotational constants were much closer to the experimentally determined values compared to the MP2/6-311++G** values, and this can also be seen in Table 3.

5. Molecular structure

To obtain a best fit gas phase structure of the PhI molecule, a nonlinear least squares fit was performed using the measured rotational constants from each of the isotopologues. In the least squares fit, there were a total of 8 varied parameters in 2D Cartesian space (the plane of the molecule). From the B3LYP/aug-cc-pVQZ calculation, the structure of PhI was determined to be planar with C_{2v} symmetry and this substantially reduced the number of parameters in the fit. Due to the planar structure the coordinates for the PhI molecule were restricted to the *x*–*y* plane (same as the *a*–*b* plane). The inertial defect obtained from the experimental rotational constants of the parent isotopologue is $\Delta = -0.175$ amu Å^2, confirming that the structure of PhI is indeed planar since this experimental value is close to zero. The small negative nonzero value however indicates the presence of out of plane vibrations within the molecule [15].

The variable parameters are the *x*–*y* coordinates of the 4 unique carbon atoms (C1, C5, C6 and C7) relative to the N atom location. These are the 8 variable fit parameters. During this structure fit, the *x*–*y* coordinates of H and O atoms are fixed relative to the

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