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Microwave Spectrum of the Argon–Tropolone van der Waals Complex[†]Wei Lin,[‡] Wallace C. Pringle,[§] Stewart E. Novick,[§] and Thomas A. Blake^{*,||}

Department of Natural Sciences and Mathematics, University of Saint Mary, Leavenworth, Kansas 66048,
Department of Chemistry, Wesleyan University, Middletown, Connecticut 06459, and Pacific Northwest
National Laboratory, MS K8-88, P.O. Box 999, Richland, Washington 99352

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The rotational spectrum of the argon–tropolone van der Waals complex in the ground vibrational state has been measured in the frequency range of 6–17 GHz using a pulsed-jet, Balle–Flygare-type Fourier transform microwave spectrometer. Eighty-six transitions for the complex ($\text{Ar}-^{12}\text{C}_7\text{H}_6^{16}\text{O}_2$) were observed, assigned, and fit using a Watson *A*-reduction Hamiltonian giving the rotational and centrifugal distortion constants $A = 1080.4365(3)$ MHz, $B = 883.4943(3)$ MHz, $C = 749.0571(2)$ MHz, $\Delta_J = 2.591(2)$ kHz, $\Delta_{JK} = -3.32(1)$ kHz, $\Delta_K = 5.232(9)$ kHz, $\delta_J = 0.944(1)$ kHz, and $\delta_K = -0.028(8)$ kHz. The tunneling motion of the hydroxyl proton in the tropolone moiety is quenched in the ground electronic state by complexation with argon. The coordinates of the argon atom in the monomer's principal axis system are $a = 0.43$ Å, $b = 0.23$ Å, and $c = 3.48$ Å.

Introduction

Tropolone has been the object of intense spectroscopic and theoretical study for many years as a prototype molecule for intramolecular proton transfer.¹ The influences of vibrational and electronic excitation and isotopic substitution on the proton's tunneling motion have been examined from the microwave^{2,3} to the infrared^{4,5} to the visible.⁶ But while the monomer has been examined throughout this range, its van der Waals complexes have been studied exclusively by electronic spectroscopy where tropolone's intense $\tilde{A}^1\text{B}_2 - \tilde{X}^1\text{A}_1$ transition acts as the complexes' active chromophore.

Sekiya et al.^{7–9} have used electronic spectroscopy (not rotationally resolved) to study a number of tropolone van der Waals complexes where the ligands have included the rare gases Ar, Kr, and Xe and water, nitrogen, methane, ethane, and propane. For argon–tropolone they found the tunneling doublet separation $|\Delta'_0 - \Delta''_0|$ in its vibronic spectrum to be 18.7 cm^{-1} , which is close to their value of 19.4 cm^{-1} for the monomer.⁷ Δ'_0 is the tunneling splitting of the zero point level in the $\tilde{A}^1\text{B}_2$ state and Δ''_0 is that of the zero-point level in $\tilde{X}^1\text{A}_1$. Δ''_0 has been accurately measured to be $0.97379995(87)\text{ cm}^{-1}$ by microwave spectroscopy. More recent work by Keske et al.³ puts the value of Δ'_0 for the monomer at 19.88 cm^{-1} and, consequently, $|\Delta'_0 - \Delta''_0| = 18.9\text{ cm}^{-1}$. Since in Sekiya's work only the dipole allowed $0^+ \leftarrow 0^+$ and $0^- \leftarrow 0^-$ transitions were observed (where $+$ and $-$ refer to the symmetries of the two lowest tunneling states) and the weaker $0^+ \leftarrow 0^-$ and $0^- \leftarrow 0^+$ were not observed, there was no experimental information to determine if the tunneling splitting change relative to the

monomer is in the ground state or excited electronic state or both in the argon–tropolone complex.

By using molecular beam Fourier transform microwave spectroscopy, not only can detailed information about the structure of argon–tropolone be determined but also the nature of the proton tunneling in the complex's ground state can be determined. Previous FT-microwave work on tropolone³ has shown the sensitivity of the technique by examining the spectra of several tropolone isotopomers in natural abundance. The two lowest tunneling states of the monomer are extremely sensitive to the isotopic substitutions of heavy atoms within the molecule's ring. The off-diagonal term that describes the rotation–tunneling interaction drops significantly when one of the carbon atoms connected to the oxygen atoms is substituted by ^{13}C ; for example, whereas one of the oxygen atoms is substituted by ^{18}O , only one tunneling state can be detected in the supersonic jet.

In this work we present the first recorded microwave spectrum of argon–tropolone. The rotational and centrifugal distortion constants of the complex have been determined. The position of the argon atom with respect to the principal axis system of the (assumed) unperturbed tropolone molecule is also determined. The proton tunneling observed in the microwave spectrum of tropolone monomer seems to be quenched in this complex.

Experiment

The spectrum of argon–tropolone was measured using a pulsed-jet Fourier transform microwave spectrometer that has been described elsewhere.^{10,11} In brief, gas pulses are produced by a standard supersonic nozzle that passes through a high-Q Fabry–Perot microwave cavity tunable between 5 and 26 GHz. A macroscopic polarization is produced when a saturating pulse of microwave radiation is injected into the cavity. The microwave pulse is timed to coincide with the passage of the gas

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* Corresponding author. E-mail: ta.blake@pnl.gov. Phone: (509) 371-6131.

[‡] University of Saint Mary.

[§] Wesleyan University.

^{||} Pacific Northwest National Laboratory.

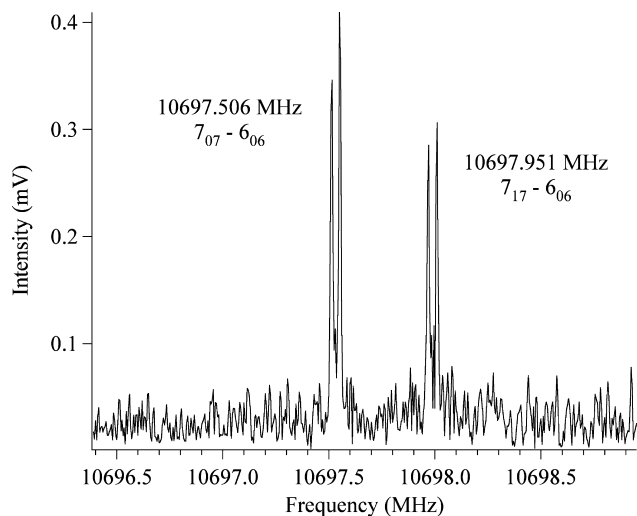


Figure 1. $7_{07}-6_{06}$ and $7_{17}-6_{06}$ pure rotational transitions of argon–tropolone. The doubling is the instrumental Doppler-doubling present in all coaxial jet-cavity FTMW spectroscopy. The spectrum was produced by Fourier transforming the signal averaged free induction decay of fifty jet pulses with five microwave pulses per gas pulse.

pulse. The resulting free induction decay (FID) is digitized and Fourier transformed to obtain a frequency spectrum. The spectrometer uses a “parallel” configuration to increase the sensitivity and resolution. This arrangement also gives rise to Doppler splitting in the observed spectra so that each transition appears as a doublet. The spectra were measured in the frequency range 6–17 GHz and the full-width-half-maximum (fwhm) of the observed lines was around 5–7 kHz. With this fwhm, we can estimate peak centers, on most transitions, to within 1 kHz.

Tropolone (98%, Aldrich) was heated to 40 °C in a copper tube and expanded with argon through a pulsed nozzle (0.5 mm diameter) operating at 10 Hz. The backing pressure was approximately 0.2 atm. The rotational temperature of the jet is estimated to be less than 5 K.

Results

The initial spectral search was carried out in the region 8.7–13.7 GHz. The transitions belonging to tropolone monomer, its isotopomers, and those from tropolone–water complex were excluded, and those remaining were considered to be argon–tropolone candidate transitions. Figure 1 shows an example of two transitions of argon–tropolone in the 10.7 GHz region. Thirteen of these transitions were found for the argon–tropolone complex, and a least-squares fit of these using SPFIT¹² allowed us to determine a preliminary set of rotational and centrifugal distortion constants. On the basis of these, a total of eighty-six *a*- and *b*-type transitions were measured in the region 6–17 GHz. Using a Hamiltonian in an *I* representation, Watson *A*-reduction, three rotational constants and five quartic centrifugal distortion constants for the ground state were fit to these 86 transitions. The assigned transitions have J'' values ranging from 2 to 8; the maximum K_a'' and K_c'' are 5 and 8, respectively. The measured transition frequencies, assignments and observed minus calculated frequencies are listed in Table 1. Table 2 contains the spectroscopic constants determined from the fit.

The fit of tropolone monomer requires a constant F , which is the coefficient in the tunneling-rotation interaction term, $F(J_a J_b + J_b J_a)$. Fitting all ¹²C tropolone monomer microwave transitions

with F set to zero will increase the root mean square (rms) from 1.5 kHz to 13.6 MHz, and increase those of ¹³C substituted C₅, C₄₍₆₎, C₃₍₇₎, and C₁₍₂₎ to be 5.19 MHz, 0.687 MHz, 0.234 MHz, 11.2 kHz, respectively (see Figure 2 for the numbering of the carbons in the ring). Unlike tropolone monomer, the argon–tropolone complex showed no evidence of tunneling splitting. The rms of the fit of the argon–tropolone ground state transitions is 4 kHz without the tunneling-rotation interaction term, which is within the experimental error of 5 kHz set in the fit. Unfortunately, we were unable to measure the ¹³C isotopomers of the argon tropolone complex in natural abundance because the signals of argon–tropolone are much weaker than those of tropolone monomer.

The vibrationally averaged position of argon is calculated using the “extreme”¹³ Kraitchman equations. Assuming there is an argon atom of zero mass in the same position as in the complex, we can apply Kraitchman equations¹⁴ to determine the argon position in the principal axis system (PAS) of the monomer. In this PAS coordinate system of the all ¹²C monomer, the argon position is $a = 0.43$ Å, $b = 0.23$ Å, and $c = 3.48$ Å. Only the absolute value of the substitution coordinates are derived using this method. The vibrational averaging in the complex and monomer are assumed to be the same which is not a very good approximation. From our results in other argon–ring complexes, the most reasonable position for the argon is toward the oxygens from the center of mass of the monomer tropolone as shown in Figure 2. This is due to the interaction of the argon with the most positive part of the ring acting as a Lewis base. From these coordinates we can calculate the distance from the center of mass to the monomer to the argon, R_{cm} , to be 3.51 Å. The angle between the positive *c*-axis and the vector connecting the tropolone center of mass and the argon, ϕ , is 7.98° and the angle between the positive *a*-axis and the projection of the aforementioned vector on the *a*, *b* plane, θ , is 28.1°. See Figures 2 and 3.

Discussion

From their electronic spectra, Sekiya et al.^{7–9} conclude that the rare gas atoms (Ar, Kr, Xe) sit above the plane of the tropolone ring in their respective clusters based on the observation that the band origin red shift of the Rg₂–tropolone complexes are approximately twice that of the Rg₁–tropolone complexes. The vibrational structure of their observed electronic spectra of the Rg₁–tropolone complexes can also be easily explained by assuming three van der Waals modes: a symmetric stretch of the rare gas atom and the monomer, a symmetric bend of the atom over the plane and an asymmetric bend of the atom over the plane. Using a model that calculates the tropolone rare gas binding energy from the sum of effective atom–atom Lennard-Jones pair potentials and with the structure of the monomer fixed at its X-ray diffraction value, the rare gas to ring distances of the Ar, Kr, and Xe complexes were calculated to be 3.36, 3.44, and 3.68 Å, respectively. Our value of 3.51 Å for the argon-to-tropolone distance compares well their estimate of 3.36 Å.

Examining the trends in the band origin red shifts for the Ar, Kr, Xe–tropolone complexes relative to that of the monomer, Sekiya et al.^{7–9} noted that these shifts are proportional to the polarizabilities of the rare gases; the changes in the tunneling splittings of the complexes, however, do not track with polarizability of the rare gases, suggesting that the tunneling of the complexes is not affected by the binding energy between the rare gas atoms and tropolone. Rather, the biggest changes in tunneling splitting are due to interactions that affect tropolo-

TABLE 1: Measured Frequencies for Ar–Tropolone in MHz

J'	K_a'	K_c'	J''	K_a''	K_c''	frequency	$o-c^a$
4	0	4	3	1	3	6172.129	0
3	3	1	2	2	0	6195.725	-4
4	1	4	3	0	3	6236.673	0
3	3	0	2	2	1	6256.845	-3
4	2	3	3	1	2	6918.341	-3
5	0	5	4	1	4	7691.056	0
5	1	5	4	0	4	7713.223	0
4	3	2	3	2	1	7735.723	-4
4	3	1	3	2	2	8026.241	-4
5	2	4	4	1	3	8311.306	-2
4	4	1	3	3	0	8379.106	-2
4	4	0	3	3	1	8393.655	1
5	3	3	4	2	2	9180.787	-4
6	0	6	5	1	5	9196.062	0
6	1	6	5	1	5	9197.636	0
6	0	6	5	0	5	9201.386	0
6	1	6	5	0	5	9202.960	0
6	2	4	5	3	3	9419.322	1
6	1	5	5	2	4	9540.342	-1
6	2	5	5	2	4	9590.942	-1
6	1	5	5	1	4	9665.192	-2
6	2	5	5	1	4	9715.792	-2
6	3	4	5	3	3	9857.909	2
6	4	3	5	4	2	9938.722	1
5	3	2	4	2	3	9959.290	-1
6	4	2	5	4	1	10010.529	0
6	2	4	5	2	3	10110.740	-3
6	3	3	5	3	2	10191.108	1
5	5	1	4	4	0	10545.240	6
5	5	0	4	4	1	10548.137	7
6	3	4	5	2	3	10549.328	-1
7	0	7	6	1	6	10695.931	0
7	1	7	6	1	6	10696.377	0
7	0	7	6	0	6	10697.506	1
7	1	7	6	0	6	10697.951	0
7	1	6	6	2	5	11089.745	-2
7	2	6	6	2	5	11107.904	0
7	1	6	6	1	5	11140.346	-1
7	2	6	6	1	5	11158.504	0
7	2	5	6	3	4	11208.703	-4
7	3	5	6	3	4	11441.248	1
6	4	3	5	3	2	11497.153	-3
7	4	4	6	4	3	11596.142	5
7	5	3	6	5	2	11601.886	1
7	2	5	6	2	4	11647.289	-4
6	4	2	5	3	3	11847.622	-3
7	3	5	6	2	4	11879.835	2
7	3	4	6	3	3	11914.460	-1
6	5	2	5	4	1	12180.016	-2
8	0	8	7	1	7	12194.055	0
8	1	8	7	1	7	12194.178	1
8	0	8	7	0	7	12194.501	1
8	1	8	7	0	7	12194.623	1
6	5	1	5	4	2	12205.436	-2
8	1	7	7	2	6	12607.225	-3
8	2	7	7	2	6	12613.246	-2
8	1	7	7	1	6	12625.383	-2
8	2	7	7	1	6	12631.405	0
6	6	1	5	5	0	12706.040	17
6	6	0	5	5	1	12706.563	18
8	2	6	7	3	5	12888.857	-9
7	4	4	6	3	3	12902.189	2
8	3	6	7	3	5	12992.933	1
8	2	6	7	2	5	13121.401	-4
8	3	6	7	2	5	13225.478	6
8	4	5	7	4	4	13229.062	7
8	5	4	7	5	3	13282.444	11
8	5	3	7	5	2	13355.526	12
8	3	5	7	3	4	13560.100	-6
8	4	4	7	4	3	13576.207	2
9	0	9	8	1	8	13691.559	1

TABLE 1: Continued

J'	K_a'	K_c'	J''	K_a''	K_c''	frequency	$o-c^a$
9	1	9	8	0	8	13691.713	0
7	5	3	6	4	2	13771.371	-4
7	4	3	6	3	4	13772.391	-1
7	5	2	6	4	3	13889.873	-2
9	1	8	8	2	7	14111.161	-3
9	2	8	8	1	7	14119.075	-1
8	4	5	7	3	4	14216.790	9
7	6	2	6	5	1	14350.698	-2
7	6	1	6	5	2	14356.329	-2
8	5	4	7	4	3	15271.138	4
8	5	3	7	4	4	15649.254	1
8	6	3	7	5	2	15979.191	-8
8	6	2	7	5	3	16011.391	-8
8	7	2	7	6	1	16512.321	-6
8	7	1	7	6	2	16513.451	-5

^a Observed minus calculated frequencies in kHz.

TABLE 2: Spectroscopic Constants for Ar–Tropolone

A/MHz	1080.4365(3)
B/MHz	883.4943(3)
C/MHz	749.0571(2)
Δ_J/kHz	2.591(2)
Δ_{JK}/kHz	-3.32(1)
Δ_K/kHz	5.232(9)
δ_J/kHz	0.944(1)
δ_K/kHz	-0.028(8)
N	86
σ/kHz	4

ne's tunneling coordinate: the tropolone–N₂ complex, for example, shows a dramatic drop in tunneling splitting compared to the rare gas complexes and this is thought to be caused by the anisotropic polarizability of the nitrogen interacting with some of the normal coordinates of tropolone that in turn couple

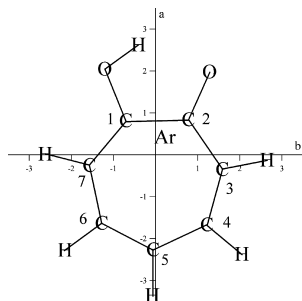


Figure 2. Structure of argon–tropolone as seen in the a, b principal axes plane. The coordinates are based on the monomer's principal axes.

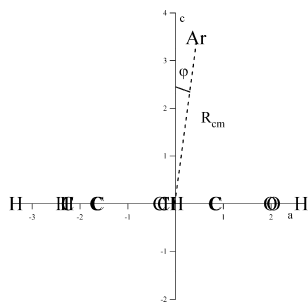


Figure 3. Structure of argon–tropolone as seen in the c, a principal axes plane. The coordinates are based on the monomer's principal axes. R_{cm} is the distance from the center of mass of the monomer to the argon atom and ϕ is the angle between the positive c -axis and R_{cm} .

with the tunneling coordinate. Of course in these electronic spectra,^{7–9} the tunneling splittings involve the ground electronic state and the S₁ state inversions, in which the latter is much larger than the former.

The ground inversion transitions observed in the tropolone monomer in its ground electronic state, S₀, and the vibration–rotational perturbations between these inversion–rotational levels³ are not observed in any of the 86 transitions that we have assigned and fit in the argon–tropolone van der Waals complex. Since our resolution is under 5 kHz and the inversion frequency was 29193.796 MHz in the monomer, the inversion has been completely quenched in the argon complex. The proton is most probably not undergoing the inversion transfer vibration that has been so important in the tropolone monomer. Through either a mass effect or a perturbation of the symmetric double minimum, the argon van der Waals force has quenched the inversion. In ref 3, we found that in the monomer the inversion was observed in the ¹⁶O–H ↔ ¹⁶O, and ¹⁶O–D ↔ ¹⁶O tropolone, but not observed in the ¹⁸O–H ¹⁶O isotopologue. This is an example of how a mass difference can also quench inversion.

Conclusions

Microwave spectra of argon–tropolone van der Waals complex in the ground vibrational state have been measured by pulsed Fourier transform microwave spectroscopy. The rotational constants and centrifugal distortion constants were determined for the first time. The rotational constants of argon–tropolone are $A = 1080.4365(3)$ MHz, $B = 883.4943(3)$ MHz, and $C = 749.0571(2)$ MHz. The coordinates of the argon in the monomer's principal axis systems are $a = 0.43$ Å, $b = 0.23$ Å, and $c = 3.48$ Å. The tunneling–rotation frequency shifts observed in tropolone monomer are not observed in the van der Waals complex. Thus, the intramolecular proton tunneling in tropolone is quenched by forming the argon tropolone complex.

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