

Hindawi Publishing Corporation
Journal of Atomic, Molecular, and Optical Physics
Volume 2012, Article ID 363247, 9 pages
doi:10.1155/2012/363247

Research Article

Millimeter-Wave Rotational Spectra of *trans*-Acrolein (Propenal) (CH_2CHCOH): A DC Discharge Product of Allyl Alcohol ($\text{CH}_2\text{CHCH}_2\text{OH}$) Vapor and DFT Calculation

A. I. Jaman and Rangana Bhattacharya

Experimental Condensed Matter Physics Division, Saha Institute of Nuclear Physics, Sector 1, Block AF, Bidhannagar, Kolkata 700 064, India

Correspondence should be addressed to A. I. Jaman, aismail.jaman@saha.ac.in

Received 18 May 2012; Accepted 5 July 2012

Academic Editor: Nigel J. Mason

Copyright © 2012 A. I. Jaman and R. Bhattacharya. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Millimeter-wave rotational spectrum of *trans*-acrolein (propenal) (CH_2CHCOH) produced by applying a DC glow discharge through a low-pressure (~ 10 – 20 mTorr) flow of allyl alcohol ($\text{CH}_2\text{CHCH}_2\text{OH}$) vapor has been observed in the ground and several excited torsional states in the frequency region: 60.0–99.0 GHz. A least-square analysis of the measured and previously reported rotational transition frequencies has produced a set of rotational and centrifugal distortion constants for the ground as well as excited torsional states. Detailed DFT calculations were also carried out with various functional and basis sets to evaluate the spectroscopic constants, dipole moment, and various structural parameters of the *trans* conformer of propenal for the ground state and compared with their corresponding experimental values. A linear variation of the inertia defect values with torsional quantum number ($\nu = 0, 1, 2, 3$) demonstrates that the equilibrium configuration of *trans*-propenal is planar.

1. Introduction

The *trans* form of propenal (CH_2CHCOH) also known as *trans*-acrolein has been detected largely in absorption toward the star-forming region Sagittarius B2(N) by Hollis et al. [2] through the observation of rotational transitions using 100 m Green Bank Telescope (GBT) operating in the frequency range from 18.0 GHz to 26.0 GHz. Spectroscopic measurements in the microwave [1, 3], infrared [4], and near ultraviolet region [5, 6] have confirmed that the *trans*-form is the most abundant and stable conformer of acrolein. The first microwave study of *trans*-acrolein in the $J = 2 \leftarrow 1$, $3 \leftarrow 2$, and $4 \leftarrow 3$ a-type R-branch transitions was reported by Wagner et al. [3]. Later on, Cherniak and Costain [1] have measured both a- and b-type transitions for $J = 2 \leftarrow 1$ and $J = 3 \leftarrow 2$. First spectroscopic evidence of the existence of

the less abundant *cis*-conformer of acrolein in the gas phase was found from studies of the near ultraviolet spectrum [7, 8]. Later on, *cis*-acrolein were detected in argon matrices [9, 10] and in the gas-phase Raman spectrum [11]. The first microwave detection of the *cis* form of acrolein in the gas phase was reported by Blom and Bauder [12]. They have reported the ground state rotational, quartic centrifugal distortion constants as well as dipole moment values. Blom et al. [13] also reported the complete substitution structures of both *trans* and *cis* conformers. The dipole moment values of the *trans* and *cis*-form of acrolein have been found to be $\mu = 3.117 \pm 0.004$ D [13] and $\mu = 2.552 \pm 0.003$ D [12] respectively. Winnewisser [14] have extended the analysis of the ground state of the *trans*-form of acrolein to the millimeter-wave region up to 180.0 GHz which has yielded a set of ground state rotational and centrifugal distortion

TABLE 1: Microwave and millimeter wave rotational transition frequencies of *trans*-propenal (CH₂CHCOH) in the ground and excited torsional states (in MHz.).

Transitions						Torsional levels							
J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	$\nu = 0$		$\nu = 1$		$\nu = 2$		$\nu = 3$	
						Obs. Freq.	Obs. - cal.	Obs. Freq.	Obs. - cal.	Obs. Freq.	Obs. - cal.	Obs. Freq.	Obs. - cal.
1	0	1	0	0	0	8902.19	-.01						
2	0	2	1	0	1	17801.28	-.06						
2	1	1	1	1	0	18221.12	-.07	18258.18	-.12	18289.86	-.01		
3	0	3	2	0	2	26694.35	-.01			26824.88	.01	26895.18	.05
3	0	3	2	1	2			26765.43	-.09			27487.70	.06
3	1	2	2	1	1	27329.73	-.07	27385.58	.08	27432.89	.02	26322.50	-.07
3	1	3	2	1	2	26079.50	-.01	26165.84	-.05	26237.28	-.12		
3	2	1	2	2	0	26718.70	-.16						
3	2	2	2	2	1	26706.76	.04						
4	0	4	3	0	3			35673.16	-.09	35752.72	.17	35846.64	.15
4	1	4	3	1	3	34768.96	-.11						
7	0	7	6	0	6	62144.50 ^a	.01	62312.22 ^a	.01	62452.30 ^a	-.11		
7	1	7	6	1	6	60816.60 ^a	.04	61018.40 ^a	.02				
7	2	6	6	2	5	62290.80 ^a	-.06	62456.80 ^a	-.03	62597.20 ^a	.05	62760.10 ^a	-.02
7	2	5	6	2	4	62460.30 ^a	-.05	62624.20 ^a	-.08	62762.20 ^a	-.07	62922.30 ^a	.03
7	3	4	6	3	3	62341.20 ^a	-.01	62506.50 ^a	-.08	62648.90 ^a	.00		
7	3	5	6	3	4	62339.40 ^a	-.07	62504.80 ^a	-.04	62647.20 ^a	.03		
7	4	3	6	4	2	62331.10 ^a	.02	62496.50 ^a	-.06				
7	5	3	6	5	2			62493.40 ^a	.03				
8	0	8	7	0	7	70961.80 ^a	.00	71154.30 ^a	.10	71315.20 ^a	.04	71506.60 ^a	-.01
8	1	7	7	1	6	72820.00 ^a	-.01	72969.40 ^a	.03	73096.20 ^a	.09	73243.30 ^a	-.06
8	1	8	7	1	7	69489.80 ^a	.06	69720.40 ^a	-.12	69911.60 ^a	.01	70139.80 ^a	-.08
8	2	7	7	2	6	71179.00 ^a	.07			71529.20 ^a	.07		
8	2	6	7	2	5	71432.70 ^a	.12	71619.40 ^a	.08	71776.20 ^a	-.03	71958.30 ^a	.04
8	3	6	7	3	5	71251.50 ^a	.06	71440.40 ^a	.05				
8	3	5	7	3	4	71255.00 ^a	.08	71443.90 ^a	.07	71606.10 ^a	-.17		
8	4	4	7	4	3	71239.10 ^a	.05	71428.20 ^a	.09				
8	5	4	7	5	3			71423.10 ^a	.12				
8	6	3	7	6	2			71421.10 ^a	-.06				
9	0	9	8	0	8							80371.70 ^a	-.01
9	1	8	8	1	7	81901.20	.01	82069.50 ^a	-.01	82212.30 ^a	.06		
9	2	8	8	2	7	80062.80 ^a	.04	80276.30 ^a	-.11	80457.00 ^a	.08	80667.10 ^a	.09
9	2	7	8	2	6	80424.00 ^a	.07	80633.30 ^a	.06	80808.70 ^a	-.05	81012.40 ^a	-.08
9	3	6	8	3	5	80172.10 ^a	.05	80384.50 ^a	.04				
9	3	7	8	3	6	80165.70 ^a	.03	80378.20 ^a	.12				
9	4	5	8	4	4	80148.40 ^a	-.04	80361.10 ^a	.04				
9	5	5	8	5	4	80140.70 ^a	.08	80353.40 ^a	.06				
9	6	4	8	6	3	80137.50 ^a	-.01	80350.40 ^a	.06				
10	0	10	9	0	9	88523.30 ^a	-.01	88765.90 ^a	-.05			89211.90 ^a	-.12
10	1	9	9	1	8	90974.40 ^a	-.05						
10	1	10	9	1	9	86818.50 ^a	-.02						
10	2	8	9	2	7	89436.20 ^a	-.01	89667.83 ^a	.03	89861.60 ^a	-.02		
10	2	9	9	2	8	88941.80 ^a	-.01	89179.48 ^a	.10	89380.10 ^a	.07	89613.80 ^a	-.02
10	3	7	9	3	6	89093.20 ^a	-.01	89329.07 ^a	-.01				
10	3	8	9	3	7	89082.20 ^a	-.08						
10	4	6	9	4	5	89059.35 ^a	-.09	89295.47 ^a	-.09				
10	5	5	9	5	4	89048.30 ^a	-.01						

TABLE 1: Continued.

Transitions						Torsional levels							
J'	K'_{-1}	K'_{+1}	J''	K''_{-1}	K''_{+1}	$\nu = 0$		$\nu = 1$		$\nu = 2$		$\nu = 3$	
						Obs. Freq.	Obs. - cal.	Obs. Freq.	Obs. - cal.	Obs. Freq.	Obs. - cal.	Obs. Freq.	Obs. - cal.
10	6	4	9	6	3	89043.55 ^a	-.04						
10	7	3	9	7	2	89041.90 ^a	-.02						
10	9	1	9	9	0	89043.17 ^a	-.02						
11	0	11	10	0	10	97263.13 ^a	-.01	97531.40 ^a	-.03	97756.50 ^a	-.12	98025.70 ^a	.05
11	1	11	10	1	10	95473.05 ^a	-.03	95791.10 ^a	.01	96054.40 ^a	.14	96369.80 ^a	.04
11	2	9	10	2	8	98470.83 ^a	-.01	98724.30 ^a	-.11	98936.00 ^a	.02		
11	2	10	10	2	9	97815.59 ^a	.03	98077.10 ^a	.00			98555.60 ^a	.08
11	3	8	10	3	7	98019.04 ^a	-.02	98278.40 ^a	.05	98500.60 ^a	.03	98752.70 ^a	-.03
11	3	9	10	3	8	98001.32 ^a	.00	98260.60 ^a	.01	98482.90 ^a	-.06	98735.30 ^a	-.01
11	4	8	10	4	7			98231.70 ^a	-.08				
11	5	7	10	5	6	97957.00 ^a	.00	98216.90 ^a	-.05	98453.50 ^a	.04		
11	6	5	10	6	4	97950.28 ^a	.00			98456.20 ^a	-.01		
11	7	4	10	7	3	97947.54 ^a	.01						
11	8	3	10	8	2	97947.05 ^a	.04						
1	1	1	2	0	2	24892.58	.01						
2	1	2	3	0	3	15585.86	.01						
6	0	6	5	1	5	13444.27	.02						
7	0	7	6	1	6	23450.46	.01						
8	0	8	7	1	7	33595.68	-.01						

^aThis work, rest are from [1].

constants. Analysis of the far-infrared spectrum of *trans* acrolein in the ν_{18} fundamental and $(\nu_{17} + \nu_{18}) - \nu_{18}$ hot bands were reported by McKellar et al. [15]. Very recently, 10 μm high-resolution rotational spectral analysis of the ν_{11} , ν_{16} , ν_{14} and $\nu_{16} + \nu_{18} - \nu_{18}$ bands of *trans*-acrolein were reported by Xu et al. [16]. In all the previous works *trans*-acrolein (propenal) was either procured commercially or prepared chemically.

Production, identification, and spectroscopic characterization of new stable and transient molecules by applying a DC glow discharge through a low-pressure flow of gas or a mixture of gases inside an absorption cell have become a well-established area of research in the field of molecular spectroscopy [21]. Recently, Jaman et. al have reported analysis of the millimeter-wave rotational spectra of propyne (CH_3CCH) [22] and propynal (HCCCOH) [23] produced by DC glow discharge technique and carried out detailed DFT calculations for both the molecules to evaluate the spectroscopic constants and molecular parameters and compared them with their respective experimental values. In the present communication, we report the analysis of the ground state ($\nu = 0$) as well as several torsional excited states ($\nu = 1, 2, 3$) rotational spectra of *trans*-propenal produced by a DC glow discharge through a low-pressure flow of allyl alcohol ($\text{CH}_2\text{CHCH}_2\text{OH}$) vapor in the frequency region 60.0–99.0 GHz. Asymmetric-top $K_{-1}K_{+1}$ -structures of different $J+1 \leftarrow J$ transitions which falls under this frequency range have been observed and measured. The measured rotational transition frequencies along with the previously reported frequencies were fitted to standard

TABLE 2: Ground state rotational and centrifugal distortion constants of *trans*-propenal (CH_2CHCOH).

Constants	Global fit using microwave and millimeter wave data	DFT calculation
A (MHz.)	47353.729 ± 0.009	47532.149
B (MHz.)	4659.4894 ± 0.0004	4635.391
C (MHz.)	4242.7034 ± 0.0004	4223.524
D_J (kHz)	1.031 ± 0.001	0.983
D_{JK} (kHz)	-8.684 ± 0.006	-9.099
D_K (kHz)	361.949 ± 0.963	346.316
d_1 (kHz)	-0.1197 ± 0.0002	-0.119
d_2 (kHz)	-0.0069 ± 0.0001	-0.006
H_{JK} (Hz)	0.014 ± 0.012	
H_{KJ} (Hz)	-0.490 ± 0.021	
σ^b	0.041	
κ^c	-0.9806	
Δ^d	-0.018	
N^e	224	

^bStandard deviation of the overall fit.

^cAsymmetry parameter.

^dInertia defect $\Delta = I_c - I_b - I_a$.

^eNumber of transitions used in the fit.

asymmetric-top Hamiltonian to determine the rotational and centrifugal distortion (CD) constants for the ground as well as excited torsional states. A detailed quantum chemical

TABLE 3: Excited-state spectroscopic constants of *trans*-propenal (CH₂CHCOH).

Constants	$\nu = 1$		$\nu = 2$		$\nu = 3$	
	This work	Ref. [3]	This work	Ref. [3]	This work	Ref. [3]
A (MHz.)	45782.822 \pm 3.231		44727.881 \pm 3.873		43420.393 \pm 5.888	
B (MHz.)	4666.210 \pm 0.004	4666.19 \pm 02	4672.056 \pm 0.005	4672.10 \pm 0.02	4678.661 \pm 0.006	4678.69 \pm 0.02
C (MHz.)	4259.668 \pm 0.005	4259.66 \pm 0.02	4273.558 \pm 0.006	4273.56 \pm 0.02	4290.297 \pm 0.007	4290.29 \pm 0.02
D_J (kHz)	1.078 \pm 0.012		1.280 \pm 0.017		1.168 \pm 0.026	
D_{JK} (kHz)	-8.735 \pm 0.075		-46.831 \pm 0.112		-28.714 \pm 0.631	
σ^f	0.077		0.085		0.075	
κ^g	-0.9804		-0.9803		-0.9802	
Δ^h	-0.702		-1.212		-1.861	
N^i	43		28		20	

^fStandard deviation of the overall fit.

^gAsymmetry parameter.

^hInertia defect $\Delta = I_c - I_b - I_a$.

ⁱNumber of transitions used in the fit.

TABLE 4: Comparison of the observed inertia defect ($\Delta/u\text{\AA}^2$) values for the ground and excited torsional state (ν) of *trans*-propenal with some other molecules.

Molecules	Inertia defect ($\Delta/u\text{\AA}^2$) values			
	$\nu = 0$	$\nu = 1$	$\nu = 2$	$\nu = 3$
<i>Trans</i> -propenal ^j (CH ₂ CHCHO)	-0.018	-0.702	-1.212	-1.861
<i>o-cis</i> 3-fluorobenzaldehyde ^k (C ₆ H ₅ FCOH)	-0.078	-0.988	-1.876	-2.726
Nitrobenzene ^l (C ₆ H ₅ NO ₂)	-0.481	-1.863	-3.186	-4.470
Benzoyl fluoride ^m (C ₆ H ₅ COF)	-0.325	-1.528	-2.765	-3.963
2-Fluoropstyrene ⁿ (C ₆ H ₄ FC ₂ H ₃)	-1.215	-2.689	-3.341	-4.380

^jThis work, ^k[17], ^l[18], ^m[19], ⁿ[20].

calculation was also carried out to evaluate the spectroscopic constants, dipole moment, and the structural parameters of the *trans* conformer of propenal. Finally, the experimentally determined rotational and CD constants were compared with the best set of values obtained after a series of DFT calculations.

2. Experimental Details

The spectrometer used in the present work is basically a 50 kHz source-modulated system combined with a free space glass discharge cell of 1.5 m in length and 10 cm in diameter. The cell is fitted with two Teflon lenses at each end. A high voltage DC regulated power supply (6kV, 1300 mA) procured from Glassman, Japan was used to apply a DC voltage through a flow of low pressure precursor gases. The cell is connected with a high vacuum pump at one end and to the sample holder section through a glass port on the other.

Klystrons and Gunn diodes followed by frequency doubler (Millitech model MUD-15-H23F0 and MUD-10-LF000) have been used as radiation sources. Millimeter wave radiation was fed into the cell by a waveguide horn and Teflon lens. A similar horn and lens arrangement was used to focus the millimeter-wave power onto the detector after propagating through the cell. The output frequency of the millimeter wave radiation was frequency modulated by a bidirectional square-wave of 50 kHz [24] and the signal from the detector (Millitech model DBT-15-RP000 and DXP-10-RPFW0) was amplified by a 100 kHz tuned preamplifier and detected by a phase-sensitive lock in amplifier in the 2f mode. The output of the lock in amplifier was connected to an oscilloscope or a chart recorder for signal display. The spectrometer was calibrated by measuring standard OCS signals in the entire frequency range. After calibration, the uncertainty in frequency measurement has been estimated to be ± 0.10 MHz. A block diagram of the spectrometer is shown in Figure 1. Details of the spectrometer used have been described elsewhere [25, 26].

Propenal (CH₂CHCOH) was produced inside the absorption cell by applying a DC glow discharge through a low pressure (~ 5 – 10 mTorr) flow of allyl alcohol (CH₂CHCH₂OH) vapor. The discharge current was maintained at around 5 mA with an applied voltage of 1.0 kV. A mechanical on/off type discharge was found to be suitable to observe good signals of propenal. Signals could be observed at room temperature. However, a controlled flow of liquid nitrogen vapor through the cell helps in improving the signal intensity. The observed signals of propenal appeared as sharp lines immediately after the DC discharge was applied but started losing intensity with time.

3. Computational Method

Quantum chemical computations were performed using GAUSSIAN 09W package [27]. Density functional methods with various functionals were used to calculate the structural parameters, dipole moment, total energy (sum of electronic

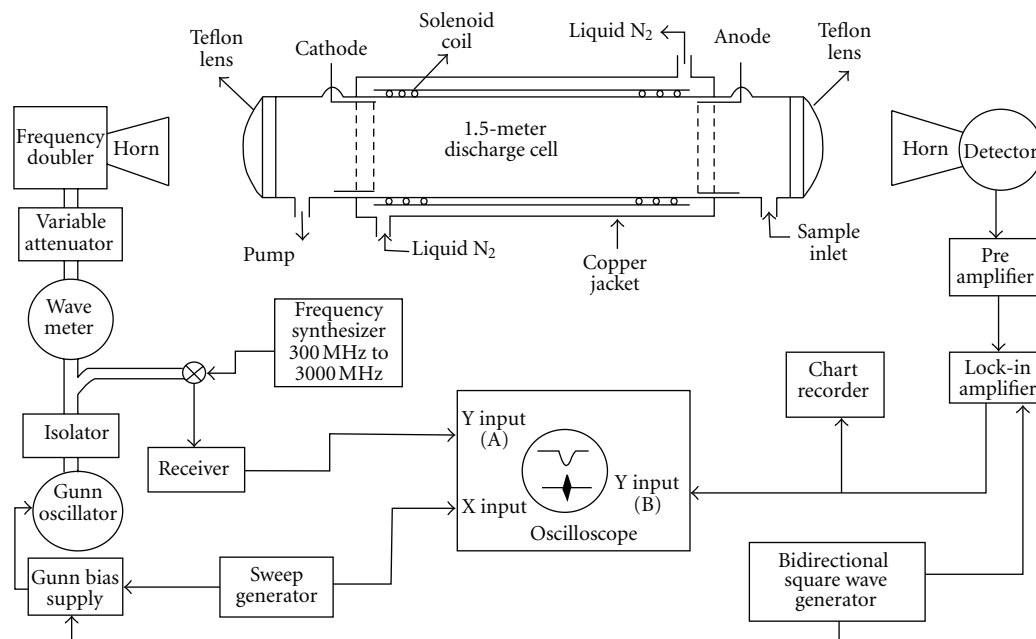


FIGURE 1: Block diagram of source-modulated millimeter wave spectrometer with DC discharge facility.

and zero point energy) as well as the rotational and centrifugal distortion constants of *trans*-propenal. The geometry optimization was carried out using different functionals like Becke 3-term correlation functional (B3LYP) with basis sets 6-31+g(d, p) to 6-311++g(d, 2p), Becke three-Parameter hybrid functional and Perdew/Wang 91 nonlocal correlation functional (B3PW91) method with different basis sets from 6-31g to 6-311++g(d, 2p), modified Perdew-Wang one-parameter hybrid model taking basis sets from 6-31g to 6-311++g(d, 2p) and Perdew, Burke, and Ernzerhof functional (PBE) with the basis sets 6-311g to 6-311++g(d, 2p). The frequency calculation along with its anharmonicity was done on optimized geometry. The objective of this DFT calculation is to compare the structural parameters and rotational constants of *trans*-propenal with the experimentally observed values in its ground state. The molecular drawing is done by using GAUSSVIEW5.0 [28].

4. Rotational Spectrum and Analysis

4.1. Ground State. The ground state rotational spectrum of the *trans* conformer of propenal was predicted in the frequency range 60.0–99.0 GHz using the rotational and centrifugal distortion constants reported earlier [14]. $J = 7 \leftarrow 6$ to $J = 11 \leftarrow 10$ series of transitions along with their different $K_{-1}K_{+1}$ components falls within this frequency range. Different components in each $J+1 \leftarrow J$ series were measured. The observed lines were found very close to their predicted values. Finally, 224 a- and b-type R- and Q-branch transitions consisting of all previous microwave [1, 3], millimeter-wave [14], and present data were used to perform a kind of global fit to the semirigid rotor Watson's S-reduction Hamiltonian (I' -representation) [29] to determine a set of three rotational, five quartic, and

two sextic centrifugal distortion constants. The shifts in frequency of the absorption lines from their rigid rotor positions due to centrifugal distortion effect were found to be less than that of propenal [23]. The observed and measured transition frequencies by us corresponding to $J = 7 \leftarrow 6$ to $11 \leftarrow 10$ series are listed in Table 1. The ground state spectroscopic constants obtained for *trans*-propenal using the global fit are listed in Table 2. The small negative value of the inertia defect ($\Delta = -0.018 \text{ u}\text{\AA}^2$) demonstrates that the equilibrium configuration of *trans*-propenal is planar. The agreement between the derived set of spectroscopic constants and those obtained earlier [1, 3, 14] with commercial samples indicates that the newly assigned transition frequencies of Table 1 definitely belong to *trans*-acrolein (*trans*-propenal), a discharge product of allyl alcohol vapor. Figure 2 shows the observed trace of the $K_{-1} = 3$ doublet of $J = 9 \leftarrow 8$ transition immediately after the DC discharge was applied. The trace remained visible for a couple of minutes on the oscilloscope screen with gradually diminishing intensity.

4.2. Excited Torsional States. From an analysis of the ultraviolet [5] and far infrared spectrum [4] of acrolein vapor the first four excited torsional levels were found to lie around 157 cm^{-1} ($\nu = 1$), 312 cm^{-1} ($\nu = 2$), 468 cm^{-1} ($\nu = 3$) and 623 cm^{-1} ($\nu = 4$), respectively. Wagner et al. [3] have reported a few low J transitions of *trans*-acrolein in the 18.0–36.0 GHz for the first three ($\nu = 1$, $\nu = 2$ and $\nu = 3$) excited torsional states and determined only the rotational constants B and C for each of these excited states. In this work, we have extended the analysis of rotational transitions in each of the above three excited states up to 99.0 GHz which has resulted in the determination of three rotational and two quartic centrifugal distortion constants for all the three torsional

TABLE 5: Calculated ground state rotational constants of *trans*-propenal (CH₂CHCOH) with various models and basis sets.

Model	Basis set	A ₀ (MHz)	B ₀ (MHz)	C ₀ (MHz)
DFT				
B3LYP	6-31+g(d, p)	47421.368	4599.276	4189.265
B3LYP	6-31++g(d, 2p)	47462.833	4596.304	4190.461
B3LYP	6-311++g(d, 2p)	47713.427	4621.512	4213.560
B3PW91	6-31g	47562.896	4564.835	4164.742
B3PW91	6-31++g(d, 2p)	47445.030	4617.117	4207.640
B3PW91	6-311++g(d, 2p)	47640.454	4642.978	4230.737
MPW1PW91	6-31g	47680.556	4583.545	4181.241
MPW1PW91	6-31++g(d, 2p)	47532.149	4635.391	4223.524
MPW1PW91	6-311++g(d, 2p)	47719.894	4660.612	4246.017
PBEPBE	6-311g	46829.581	4528.525	4119.901
PBEPBE	6-311++g(d, 2p)	46855.368	4594.974	4175.330
PBEPBE	6-31++g(d, 2p)	46605.708	4567.810	4150.825
Expt. ^o		47353.729	4659.4894	4242.7034

^oThis work.TABLE 6: Comparison of the molecular bond lengths, dipole moment, and total energy of *trans*-propenal calculated by various methods and basis sets with the experimental values.

Models	Basis sets	Bond lengths between							Dipole Moment (D)	Energy (eV)
		1C–2H	1C–3H	1C–4C	4C–5H	4C–6C	6C–7H	6C–8O		
B3LYP	6-31+g(d, p)	1.088	1.085	1.340	1.087	1.474	1.112	1.218	3.515	-5220.511
	6-31++g(d, 2p)	1.087	1.084	1.340	1.086	1.474	1.111	1.218	3.502	-5220.755
	6-311++g(d, 2p)	1.084	1.081	1.335	1.083	1.474	1.109	1.211	3.464	-5221.979
B3PW91	6-31g	1.088	1.084	1.341	1.086	1.465	1.106	1.239	3.542	-5216.647
	6-31++g(d, 2p)	1.085	1.082	1.334	1.084	1.471	1.111	1.208	3.491	-5218.334
	6-311+g(d, 2p)	1.085	1.082	1.334	1.084	1.417	1.111	1.208	3.434	-5219.694
MPW1PW91	6-31g	1.086	1.083	1.339	1.085	1.463	1.104	1.236	3.564	-5217.218
	6-31++g(d, 2p)	1.086	1.083	1.336	1.085	1.470	1.110	1.213	3.481	-5219.204
	6-311++g(d, 2p)	1.084	1.081	1.332	1.083	1.469	1.109	1.205	3.443	-5220.238
PBEPBE	6-311g	1.093	1.090	1.348	1.092	1.467	1.115	1.250	3.392	-5213.844
	6-31++g(d, 2p)	1.096	1.092	1.349	1.095	1.475	1.123	1.228	3.394	-5214.252
	6-311++g(d, 2p)	1.093	1.089	1.344	1.092	1.474	1.121	1.221	3.367	-5215.531
Expt. ^p		1.089	1.081	1.341	1.084	1.468	1.113	1.215	3.117	

^p Ref. [13].

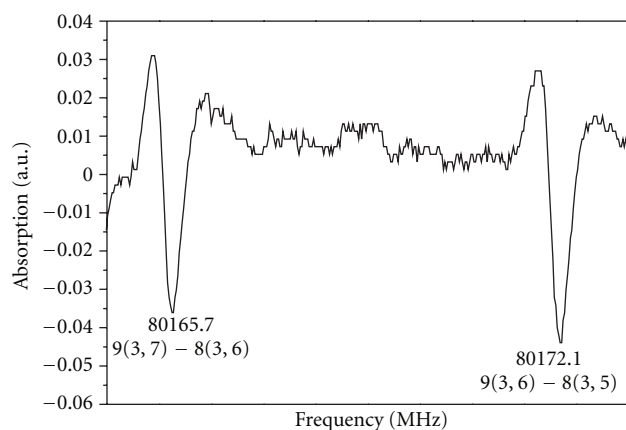
excited states. The new assigned transitions along with those reported earlier [3] are also shown in Table 1 along with the ground state transitions. The excited state data were also used to fit to the same semirigid rotor Watson's S-reduction Hamiltonian (I' -representation) [29]. Three rotational and two quartic (D_J and D_{JK}) CD constants were used to fit the data. The contribution of other CD parameters was found to be negligible while fitting the excited state data. The derived spectroscopic constants and inertia defect values for the three torsional excited states are shown in Table 3. The more negative inertia defect values for successive torsional excited states indicate that the excited state lines arise from an out-of-plane vibration, in this case, COH group torsion about C–C single bond. The observed inertia defect values for the ground and torsional excited states of *trans*-propenal and some other related molecules are compared in Table 4. The plots of inertia defect values with torsional quantum

numbers for *trans*-propenal along with other molecules are shown in Figure 3 for comparison.

4.3. Computational Results. Propenal is a slightly asymmetric prolate top molecule ($\kappa = -0.9806$). The optimization of geometry for the *trans* conformer of propenal was tested by employing various levels of theory and basis sets. However, the computed rotational and centrifugal distortion constants and the structural parameters obtained with model MPW1PW91 model with 6-31++g(d, 2p) basis set were found to be in good agreement with the observed values. Calculated values of ground state rotational constants of *trans*-propenal obtained with various models and basis sets are shown in Table 5. Results obtained with DFT MPW1PW91/6-31++g(d, 2p) have been compared with the corresponding experimental values in Table 2. For optimized geometry of *trans*-propenal the calculated energy

TABLE 7: Comparison of the molecular bond angles of *trans*-propenal calculated by various methods and basis sets with the experimental values.

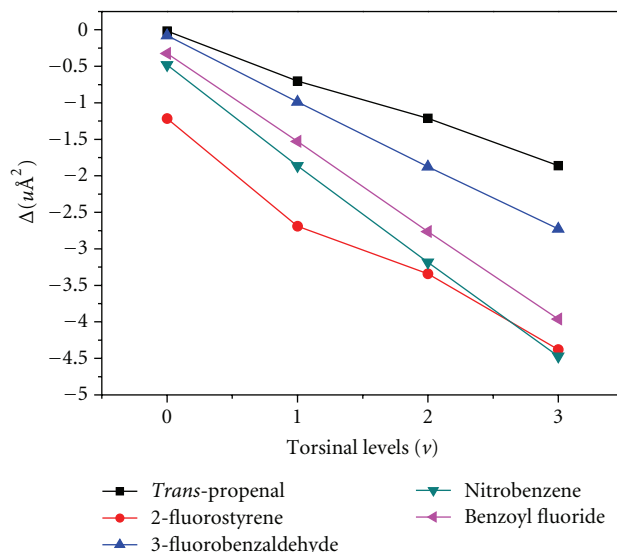
Models	Basis sets	Bond angles between								
		H2-C1-H3	H2-C1-C4	H3-C1-C4	C1-C4-H5	C1-C4-H6	H5-C4-C6	C4-C6-H7	C4-C6-O8	H7-C6-O8
B3LYP	6-31+g(d,p)	116.799	121.067	122.133	122.342	121.089	116.569	115.154	124.162	120.684
	6-31++g(d,2p)	116.834	121.043	122.123	122.314	121.153	116.533	115.123	124.165	120.712
	6-311++g(d,2p)	116.849	120.973	122.177	122.347	121.069	116.583	114.830	124.348	120.822
B3PW91	6-31g	116.488	121.219	122.22	122.091	121.314	116.596	115.381	123.994	120.626
	6-31++g(d,2p)	116.699	121.104	122.196	122.363	120.926	116.711	115.126	124.248	120.625
	6-311+g(d,2p)	116.922	120.852	122.226	122.414	120.821	116.766	114.689	124.414	120.897
MPW1PW91	6-31g	116.516	121.201	122.284	122.146	121.259	116.594	115.443	123.945	120.612
	6-31++g(d,2p)	116.938	120.930	122.131	122.419	120.864	116.717	115.023	124.176	120.800
	6-311++g(d,2p)	116.964	120.807	122.227	122.491	120.714	116.794	114.691	124.394	120.914
PBEPBE	6-311g	116.573	121.132	122.295	122.136	121.724	116.139	115.404	123.451	120.604
	6-31++g(d,2p)	116.976	120.764	122.260	122.329	120.985	116.685	114.796	124.334	120.870
	6-311++g(d,2p)	116.998	120.664	122.337	122.394	120.846	116.762	114.486	124.549	120.964
Expt. ^a		118.0	119.8	122.2	122.4	120.3	117.3	114.7	123.9	121.3

^aRef. [13].FIGURE 2: Observed trace of the $K_{-1} = 3$ doublet of $J = 9-8$ transition of *trans*-propenal produced by DC discharge.

is -5219.204 eV and the dipole moment is 3.481 D. The number and labeling of atoms in propenal molecule as shown in Figure 4. Bond lengths and angles have been computed using different models and basis sets and are shown in Tables 6 and 7, respectively.

5. Conclusion

An efficient method of generating *trans*-propenal (*trans*-acrolein) in the gas phase by applying a DC glow discharge through a low pressure vapor of allyl alcohol inside the absorption cell has been presented. The gas phase rotational spectra of the *trans* conformer of propenal produced in this way has been recorded and analyzed in the frequency range 60.0–99.0 GHz for the ground as well as three torsional excited states ($\nu = 1, 2$ and 3). The asymmetric top $K_{-1}K_{+1}$ -components of different transitions having J values 6 to 10 have been measured. The observed transition frequencies

FIGURE 3: Plot of the variation of inertia defect values with torsional state quantum number for *trans*-propenal and some other molecules.

along with the previously reported data [1, 3, 14] were fitted to a standard asymmetric-top Watson's S-reduction Hamiltonian (I' -representation) to determine ground state rotational and centrifugal distortion constants. Analysis of the rotational transitions for the three excited torsional states has been extended up to 99.0 GHz which has enabled us to determine the three rotational and two centrifugal distortion constants. The small negative value of the inertia defect ($\Delta = -0.018$ $u\text{\AA}^2$) in the ground vibrational state ($\nu = 0$) and the linear variation of the inertia defect values with torsional quantum number ($\nu = 1, 2, 3$) demonstrate that the equilibrium configuration of *trans*-propenal is planar as noticed in case of 3-fluorobenzaldehyde, benzoyl fluoride,

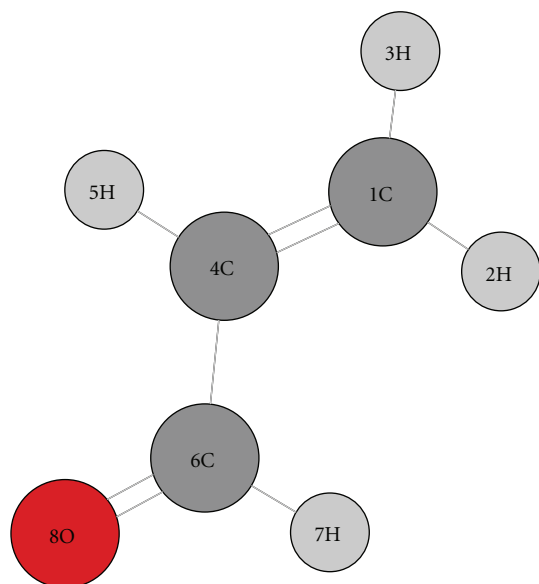


FIGURE 4: Optimized geometry of *trans*-propenal molecule and the numbering of atoms

and nitrobenzene (Figure 4). The existence of a slightly bent or twisted-COH group would have resulted in a zig-zag behavior in the variation of inertia defect values with torsional quantum number as observed in the case of 2-fluorostyrene (Figure 4). To compare the experimental results with theory, DFT calculations were performed using various models and basis sets. However, it was found that MPW1PW91 model with 6-31++g (d, 2p) basis set produced the best values of rotational and quartic centrifugal distortion constants which are close to the experimental values.

Acknowledgment

The authors would like to thank Mr. A. K. Bhattacharya for his technical assistance during the course of this work.

References

- [1] E. A. Cherniak and C. C. Costain, "Microwave spectrum and molecular structure of *trans*-acrolein," *The Journal of Chemical Physics*, vol. 45, no. 1, pp. 104–110, 1966.
- [2] J. M. Hollis, P. R. Jewell, F. J. Lovas, A. Remijan, and H. Møllendal, "Green bank telescope detection of new interstellar aldehydes: propenal and propanal," *Astrophysical Journal*, vol. 610, no. 1, pp. L21–L24, 2004.
- [3] R. Wagner, J. Fine, J. W. Simmons, and J. H. Goldstein, "Microwave spectrum, structure, and dipole moment of *s*-*trans* acrolein," *The Journal of Chemical Physics*, vol. 26, no. 3, pp. 634–637, 1957.
- [4] R. K. Harris, "Vibrational assignments for glyoxal, acrolein and butadiene," *Spectrochimica Acta*, vol. 20, no. 7, pp. 1129–1141, 1964.
- [5] J. C. D. Brand and D. G. Williamson, "Near-ultra-violet spectrum of propenal," *Discussions of the Faraday Society*, vol. 35, pp. 184–191, 1963.
- [6] J. M. Hollas, "The electronic absorption spectrum of acrolein vapour," *Spectrochimica Acta*, vol. 19, no. 9, pp. 1425–1426, E1–E2, 1427–1441, 1963.
- [7] A. C. P. Alves, J. Christoffersen, and J. M. Hollas, "Near ultra-violet spectra of the *s*-*trans* and a second rotamer of acrolein vapour," *Molecular Physics*, vol. 20, no. 4, pp. 625–644, 1971.
- [8] A. C. P. Alves, J. Christoffersen, and J. M. Hollas, "Erratum to "Near ultra-violet spectra of the *s*-*trans* and a second rotamer of acrolein vapour";," *Molecular Physics*, vol. 21, no. 2, p. 384, 1971.
- [9] A. Krantz, T. D. Goldfarb, and C. Y. Lin, "A simple method for assigning vibrational frequencies to rapidly equilibrating rotational isomers," *Journal of the American Chemical Society*, vol. 94, no. 11, pp. 4022–4024, 1972.
- [10] C. E. Blom, R. P. Miller, and H. Günthard, "*S*-*trans* and *S*-*cis* acrolein: trapping from thermal molecular beams and uv-induced isomerization in argon matrices," *Chemical Physics Letters*, vol. 73, pp. 483–486, 1980.
- [11] L. A. Carreira, "Raman spectrum and torsional potential function of acrolein," *Journal of Physical Chemistry*, vol. 80, no. 11, pp. 1149–1152, 1976.
- [12] C. E. Blom and A. Bauder, "Microwave spectrum, rotational constants and dipole moment of *s*-*cis* acrolein," *Chemical Physics Letters*, vol. 88, no. 1, pp. 55–58, 1982.
- [13] C. E. Blom, G. Grassi, and A. Bauder, "Molecular structure of *s*-*cis*- and *s*-*trans*-acrolein determined by microwave spectroscopy," *Journal of the American Chemical Society*, vol. 106, no. 24, pp. 7427–7431, 1984.
- [14] M. Winnewisser, G. Winnewisser, T. Honda, and E. Hirta, "Ground state centrifugal distortion constants of *trans*-acrolein, CH₂=CH-CHO from the microwave and millimeter wave rotational spectra," *Zitschrift, Naturforsch*, vol. 30, pp. 1001–1014, 1975.
- [15] A. R. W. McKellar, D. W. Tokaryk, and D. R. T. Appadoo, "The far-infrared spectrum of acrolein, CH₂CHCHO: the ν_{18} fundamental and ($\nu_{17} + \nu_{18}$)— ν_{18} hot bands," *Journal of Molecular Spectroscopy*, vol. 244, no. 2, pp. 146–152, 2007.
- [16] L.-H. Xu, X. Jiang, H. Shi et al., "10 μ m High-resolution spectrum of *trans*-acrolein: rotational analysis of the ν_{11} , ν_{16} , ν_{14} and $\nu_{16} + \nu_{18}$ — ν_{18} bands," *Journal of Molecular Spectroscopy*, vol. 268, no. 1-2, pp. 136–146, 2011.
- [17] J. L. Alonso and R. M. Villamañán, "Rotational isomerism in monofluorobenzaldehydes," *Journal of the Chemical Society, Faraday Transactions*, vol. 85, no. 2, pp. 137–149, 1989.
- [18] J. H. Høg, L. Nygaard, and G. Ole Sørensen, "Microwave spectrum and planarity of nitrobenzene," *Journal of Molecular Structure*, vol. 7, no. 1-2, pp. 111–121, 1971.
- [19] R. K. Kakar, "Microwave spectrum of benzoyl fluoride," *The Journal of Chemical Physics*, vol. 56, no. 3, pp. 1246–1252, 1972.
- [20] R. M. Villamañán, J. C. López, and J. L. Alonso, "On the planarity of 2-fluorostyrene," *Journal of the American Chemical Society*, vol. 111, no. 17, pp. 6487–6491, 1989.
- [21] S. Saito, "Laboratory microwave spectroscopy of interstellar molecules," *Applied Spectroscopy Reviews*, vol. 25, pp. 261–296, 1989.
- [22] A. I. Jaman, P. Hemant Kumar, and P. R. Bangal, "Rotational spectrum of propyne observed in a DC glow discharge and DFT calculation," *Asian Journal of Spectroscopy, Special Issue*, pp. 43–48, 2010.
- [23] A. I. Jaman, R. Bhattacharya, D. Mondal, and A. Kumar Das, "Millimeterwave spectral studies of propynal (HCCCCHO) produced by DC discharge and ab initio DFT calculation,"

- Journal of Atomic, Molecular, and Optical Physics*, vol. 2011, Article ID 439019, 8 pages, 2011.
- [24] J. F. Verdick and C. D. Cornwell, "Radio-frequency spectrometer with bidirectional square wave frequency modulation," *Review of Scientific Instruments*, vol. 32, no. 12, pp. 1383–1386, 1961.
- [25] A. I. Jaman, "Millimeterwave spectroscopy of transient molecules produced in a DC discharge," *Pramana*, vol. 61, no. 1, pp. 85–91, 2003.
- [26] A. I. Jaman, "Millimeter wave spectrum of ICN, a transient molecule of chemical and astrophysical interest," *Journal of Physics*, vol. 80, no. 1, Article ID 012006, 2007.
- [27] M. J. Frisch, G. W. Trucks, and H. B. Schlegel, *Gaussian 09, Revision A. 1*, Gaussian, Wallingford, Conn, USA, 2009.
- [28] GaussView 5. 0.
- [29] J. K. G. Watson, "Aspects of quartic and sextic centrifugal effects on rotational energy levels," in *Vibrational Spectra and Structure*, J. R. Durig, Ed., vol. 6, pp. 1–89, MerceL Dekker, New York, NY, USA, 1977.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

