

The Rotational Spectrum of Propene: Internal Rotation Analysis and *ab Initio* and Experimental Centrifugal Distortion Constants

G. WŁODARCZAK,*¹ J. DEMAISON,* N. HEINEKING,† AND A. G. CSÁSZÁR‡

*Laboratoire de Spectroscopie Hertzienne, URA CNRS 249, Université de Lille 1, 59655 Villeneuve d'Ascq, France; †Abteilung Chemische Physik, Institut für Physikalische Chemie der Universität Kiel, Olshausenstrasse 40-60, D-2300 Kiel 1, Germany; and ‡Department of Theoretical Chemistry, Eötvös University, H-1518 Budapest 112, P.O. Box 32, Hungary

Following the measurement of the rotational spectrum of propene in the microwave and millimeterwave regions, internal rotation and centrifugal distortion analysis is performed. A scaled quantum mechanical force field is calculated, and the theoretical centrifugal distortion constants, calculated from this force field, are compared to the experimental ones. © 1994 Academic Press, Inc.

INTRODUCTION

The ground state microwave (MW) spectrum of propene, $\text{CH}_3\text{-CH}=\text{CH}_2$, was first investigated up to 40 GHz by Lide and Mann (1) for the normal species and one ^{13}C isotopomer. The internal axis method (IAM) was used to analyze the splittings due to the internal rotation of the methyl group and the threefold barrier height, V_3 , was determined. The molecular dipole moment also was measured ($\mu_a = 0.360(1)$ and $\mu_b = 0.05(2)$ D), and an approximate structure was derived. Further studies in the microwave region were undertaken with deuterated (2–4) and ^{13}C (3) isotopomers. The rotational spectra in the torsional excited states ($\nu_t = 1, 2$) were analyzed by Hirota *et al.* (5–7) for the normal and some deuterated isotopomers. In particular, they analyzed the internal rotation in $\text{CH}_2\text{D-CH}=\text{CH}_2$, where the top is asymmetric. The three- and sixfold barriers, V_3 and V_6 , have been determined.

The torsional spectra were investigated in the far-infrared (FIR) region at low resolution and the transitions $\nu = 1-0$ and $\nu = 2-1$ were measured by various authors (8–11). Combined analysis of MW and FIR data allowed an improved determination of the barrier height. More recently, the FIR spectrum was recorded with higher resolution and *ab initio* calculations were performed at the double-zeta (DZ) restricted Hartree–Fock (RHF) level to determine V_3 and V_6 (12). Other *ab initio* torsional potential calculations have been made at the 6-31G (*d, p*) RHF and MP2 level for propene, taking into account the molecular relaxation during rotation of the methyl group (13). The rotational Zeeman effect was analyzed, resulting in accurate molecular *g*-values (14).

A new analysis of the structure was recently published by Harmony and co-workers (15) using scaled moments of inertia. These authors concluded that the hydrogen atom coordinates were not reliable because the available value of the rotational constant *A* was highly inaccurate.

¹ E-mail: gwlodarc@lsh.univ-lille1.fr.

TABLE I

Ground State Rotational Transitions for Propene (in MHz)

J	K-	K+	J	K-	K+	A obs.	c-o	E obs.	c-o
30	5	25	30	5	26	8072.142	-0.017	8073.789	0.036
9	2	7	9	2	8	8586.710	0.035	8588.640	-0.270
6	2	4	7	1	7	9447.529	-0.002	9408.512	-0.025
16	3	13	16	3	14	9845.236	0.011	9848.445	0.000
26	7	20	27	6	21	10369.950	0.031	10357.396	0.033
26	7	20	26	7	22			10539.858	0.022
26	7	19	27	6	22	10555.382	0.029	10591.254	-0.037
26	7	19	27	6	21			10408.793	0.005
4	1	3	4	1	4	11708.499	-0.007	11707.219	-0.005
24	5	20	23	6	17	12161.255	0.008	12164.178	-0.038
10	2	8	10	2	9	12592.450	0.002	12594.410	-0.166
17	3	14	17	3	15	13687.190	0.020	13691.200	-0.129
3	0	3	2	1	2	16367.680	0.072	16382.240	0.090
4	2	3	5	1	4	16901.200	0.207	16856.490	-0.058
5	1	4	5	1	5	17554.970	0.034	17553.020	-0.064
11	2	9	11	2	10	17688.220	0.020	17690.370	-0.100
18	3	15	18	3	16	18550.810	0.088	18555.610	-0.068
5	2	3	6	1	6	21632.430	-0.149	21594.510	0.057
12	2	10	12	2	11	23954.230	0.045	23956.640	-0.103
19	3	16	19	3	17	24556.410	0.140	24562.050	-0.020
6	1	5	6	1	6	24557.850	0.036	24555.020	-0.072
7	1	6	6	2	5	25149.890	-0.058	25187.870	0.051
25	7	19	26	6	20	28695.467	-0.008	28681.549	-0.037
25	7	19	26	6	21			28799.761	-0.051
25	7	18	26	6	21	28814.337	-0.003	28852.487	0.020
25	7	18	26	6	20			28734.282	0.033
27	4	23	27	4	24	28817.615	0.044	28823.552	-0.065
25	5	21	24	6	18	30536.012	-0.005	30539.387	0.005
13	2	11	13	2	12	31438.773	0.023	31441.207	0.018
25	5	20	24	6	19	32040.886	0.005	32048.729	0.041
8	1	6	7	1	7	32702.928	-0.011	32696.957	-0.004
13	3	5	9	2	8	33088.901	0.051	33053.938	-0.020
13	1	13	12	2	10	33265.160	0.048	33204.581	0.016
15	1	15	14	2	12	33441.829	0.011	33481.721	-0.053
2	1	2	1	1	1	33707.814	-0.011	33708.770	-0.009
14	1	14	13	2	11	34279.090	0.029	34318.663	-0.029
2	0	2	1	0	1	34851.529	-0.006	34851.273	-0.018
4	0	4	3	1	3	35307.002	-0.010	35320.993	0.001
2	1	1	1	1	0	36050.194	-0.015	36049.289	-0.018
3	2	2	4	1	3	37163.613	0.020	37106.805	-0.019
1	1	0	1	0	1	38155.730	0.011	38141.503	-0.007
7	0	7	6	0	6	120582.480	-0.001	120581.400	-0.022
7	6	1	6	6	0	122157.846	-0.055	122158.783	-0.116
7	5	2	6	5	1	122173.991	-0.052	122174.608	-0.026
7	4	4	6	4	3	122209.425	-0.027	122210.733	-0.029
7	3	5	6	3	4	122273.812	-0.036	122288.187	-0.023
7	3	4	6	3	3	122324.012	-0.045	122309.658	0.099
7	2	5	6	2	4	123341.683	-0.015	123340.798	-0.023
10	7	3	9	7	2	174536.549	-0.072	174537.150	-0.064
10	7	4	9	7	3	174536.549	-0.073	174538.090	-0.052
10	6	4	9	6	3	174564.226	-0.033	174565.580	-0.099
10	5	6	9	5	5	174617.801	-0.093	174619.410	-0.042
10	5	5	9	5	4	174617.801	0.013	174618.669	-0.003
10	4	7	9	4	6	174723.224	-0.020	174728.366	0.017
10	4	6	9	4	5	174731.543	-0.040	174727.971	-0.027
10	3	8	9	3	7	174839.537	-0.022	174843.418	-0.002
13	9	5	12	9	4	226900.198	-0.039	226900.998	-0.104
13	9	4	12	9	3	226900.198	-0.037	226898.966	-0.089
13	7	6	12	7	5	226959.003	-0.005	226959.859	-0.004
13	7	7	12	7	6	226959.003	-0.004	226961.031	0.010
13	6	7	12	6	6	227026.708	0.026	227028.483	-0.024
13	5	8	12	5	7	227150.934	-0.020	227151.326	0.117
13	4	10	12	4	9	227370.242	0.028	227379.632	0.034
13	4	9	12	4	8	227424.711	0.034	227417.374	0.067
13	1	12	11	1	11	231223.292	0.071	231220.504	0.042
13	2	11	12	2	10	232586.859	0.087	232585.927	0.107
14	0	14	13	0	13	232571.429	0.086	232569.682	0.054
14	9	6	13	9	5	244365.558	0.035	244366.421	-0.016
14	9	5	13	9	4	244365.558	0.036	244364.251	-0.015
14	6	8	13	6	7	244529.608	0.046	244531.542	-0.019
14	5	10	13	5	9	244684.219	0.050	244687.690	0.069
15	0	15	14	1	14	244761.821	0.073	244764.876	0.234
14	4	11	13	4	10	244950.991	-0.073	244957.729	0.042
14	4	10	13	4	9	245042.849	0.050	245038.242	0.056

This communication describes new microwave measurements, using the microwave Fourier transform (MWFT) technique, and extends the measurements to the millimeterwave range in order to improve the accuracy of the determination of the rotational constant A . Based on all the available data, a centrifugal distortion and an internal rotation analysis (IAM method) is performed. To aid the analysis, an accurate ab

initio quadratic force field is generated, and the theoretical centrifugal distortion constants are compared to the experimental values.

EXPERIMENTAL AND THEORETICAL DETAILS

Propene was obtained commercially and was used without purification. The MW measurements between 120 and 250 GHz were made in Lille with a computer-controlled spectrometer using superheterodyne detection (16). The spectra were measured at room temperature and at pressures below 10 mTorr. The estimated accuracy of the measured frequencies is better than 50 kHz. The MW spectra between 8 and 40 GHz were recorded in Kiel with MWFT spectrometers (17). The estimated accuracy of these measurements is about 10 kHz.

The experimental frequencies are reported in Table I, together with the (calculated – observed) frequency values. Experimental molecular constants are given in Table II.

The quadratic force field of propene was computed for this work at the RHF self-consistent-field (SCF) level using the 4-21G basis set of Pulay *et al.* (18). The internal coordinate system was chosen as prescribed in Refs. (18, 19) and is reported in Table III. The labeling of the atoms is shown in Fig. 1. A 4-21G RHF optimized geometry of propene has been reported in Ref. (20). This geometry was corrected by small offset values following the standard procedure described in Ref. (18). This corrected geometry was used as the reference geometry for expansion of the potential energy as a function of nuclear displacements and is given in Table IV. The computed quadratic force field was then scaled (21–23) to reduce the systematic errors in the computed force field: 11 scale factors were taken over from molecules similar to propene (21). The scale factors are reported in Table III. The computed and observed fundamental wavenumbers of propene are quoted in Table V. No scaling was done for the methyl

TABLE II

Experimental Molecular Constants of Propene in the Ground State and Correlation Matrix

Global fit ^a														
A (MHz)	46281.1260 (55)	1.000												
B (MHz)	9308.3351 (11)	0.865	1.000											
C (MHz)	8130.2747 (12)	0.606	0.816	1.000										
V ₃ (cal/mol)	1956.50 (29)	-0.149	0.023	0.523	1.00									
I _α (u.Å ²)	3.16904 (17)	0.140	-0.026	-0.428	-0.881	1.000								
θ (°)	25.07956 (35)	0.179	-0.035	-0.593	-0.901	0.722	1.000							
ΔJ (kHz)	6.2596 (19)	0.696	0.764	0.609	-0.038	0.020	0.028	1.000						
ΔJK (kHz)	-40.032 (21)	0.625	0.608	0.470	-0.002	-0.002	0.006	0.892	1.000					
ΔK (kHz)	465.53 (10)	0.286	0.009	0.002	-0.045	0.048	0.064	0.120	0.085	1.000				
δJ (kHz)	1.22835 (30)	0.001	0.047	-0.042	0.029	-0.014	-0.022	0.052	0.338	0.013	1.000			
δK (kHz)	16.093 (30)	0.229	0.309	0.483	0.264	-0.224	-0.292	0.359	0.098	-0.083	-0.820	1.000		
ΦJK (Hz)	-5.48 (15)	0.269	-0.018	-0.025	-0.016	0.010	0.043	0.193	0.310	0.903	0.150	-0.119	1.000	
ΦK (Hz)	-1.058 (99)	0.151	-0.028	-0.408	-0.383	0.272	0.671	0.014	0.015	0.081	-0.004	-0.179	0.078	1.000
Fit of A lines ^{a,b}														
A (MHz)	46290.408 (43)	1.000												
B (MHz)	9305.3308 (48)	0.447	1.000											
C (MHz)	8134.2226 (43)	0.530	0.940	1.000										
ΔJ (kHz)	6.278 (11)	0.376	0.852	0.908	1.000									
ΔJK (kHz)	-23.099 (163)	0.320	0.640	0.519	0.347	1.000								
ΔK (kHz)	666.3 (23)	0.542	0.065	0.214	0.338	-0.463	1.000							
δJ (kHz)	1.2308 (28)	0.245	0.020	-0.087	-0.087	-0.131	0.455	1.000						
δK (kHz)	-27.63 (31)	-0.238	0.210	0.201	0.198	0.397	-0.599	-0.910	1.000					
ΦJK (Hz)	42.6 (21)	0.246	0.530	0.422	0.305	0.945	-0.446	-0.186	0.429	1.000				
ΦK (Hz)	1319. (30)	0.282	-0.207	-0.062	0.066	-0.729	0.912	0.414	-0.616	-0.749	1.000			

a) standard errors in parentheses are shown in units of the last digit.

b) A reduction, representation I'.

TABLE III

Internal Coordinate System and Scale Factors for Propene^a

No	Internal coordinate	Description	Scale factor 4-21G RHF ^b
1	$q_1 = R(1, 2)$	C-C stretch	0.920
2	$q_2 = R(1, 3)$	C=C stretch	0.866
3	$q_3 = R(1, 4)$	C-H stretch	0.866
4,5	$q_4 = R(3, 5)$; $q_5 = R(3, 6)$	C-H stretches	0.866
6-8	$q_6 = R(2, 7)$; $q_7 = R(2, 8)$; $q_8 = R(2, 9)$	C-H stretches	0.866
9	$q_9 = \angle(3, 1, 2)$	C-C-C bending	0.800
10	$q_{10} = \angle(4, 1, 2) - \angle(4, 1, 3)$	C-H bending	0.800
11	$q_{11} = 2 * \angle(6, 3, 5) - \angle(6, 3, 1) - \angle(5, 3, 1)$	CH ₂ bending	0.800
12	$q_{12} = \angle(6, 3, 1) - \angle(5, 3, 1)$	CH ₂ bending	0.800
13	$q_{13} = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3$	CH ₃ bending	0.765
14	$q_{14} = 2 * \alpha_3 - \alpha_1 - \alpha_2$	CH ₃ bending	0.765
15	$q_{15} = \alpha_1 - \alpha_2$	CH ₃ bending	0.765
16	$q_{16} = 2 * \beta_1 - \beta_2 - \beta_3$	CH ₃ bending	0.765
17	$q_{17} = \beta_2 - \beta_3$	CH ₃ bending	0.765
18	$q_{18} = 1$ out of (2, 1, 3) plane	Out of plane CH ₂ bending	0.730
19	$q_{19} = \phi_1 + \phi_2 + \phi_3 + \phi_4$	Torsion around C=C	0.776
20	$q_{20} = 4$ out of (2, 1, 3) plane	Out of plane CH bending	0.730
21	$q_{21} = \tau_1 + \tau_2 + \tau_3 + \tau_4 + \tau_5 + \tau_6$	Methyl torsion	1.0 ^c

a) All coordinates are defined as displacements from reference, with stretches in Å and angle bends in radian. See Fig. 1 for labeling of atoms. $\alpha_1 = \angle(8, 2, 7)$; $\alpha_2 = \angle(9, 2, 7)$; $\alpha_3 = \angle(8, 2, 9)$; $\beta_1 = \angle(1, 2, 7)$; $\beta_2 = \angle(1, 2, 8)$; $\beta_3 = \angle(1, 2, 9)$; $\phi_1 = \text{dihedral } \angle(5, 3, 1, 2)$; $\phi_2 = \text{dihedral } \angle(5, 3, 1, 4)$; $\phi_3 = \text{dihedral } \angle(6, 3, 1, 2)$; $\phi_4 = \text{dihedral } \angle(6, 3, 1, 4)$; $\tau_1 = \text{dihedral } \angle(7, 2, 1, 3)$; $\tau_2 = \text{dihedral } \angle(7, 2, 1, 4)$; $\tau_3 = \text{dihedral } \angle(8, 2, 1, 3)$; $\tau_4 = \text{dihedral } \angle(8, 2, 1, 4)$; $\tau_5 = \text{dihedral } \angle(9, 2, 1, 3)$; $\tau_6 = \text{dihedral } \angle(9, 2, 1, 4)$; Dihedral (a, b, c, d) is defined as the angle between the planes abc and bcd and is positive if a is in the direction of the vector product $\mathbf{cb} * \mathbf{cd}$.

b) Taken from refs. (21) and (37).

c) Not scaled, see text.

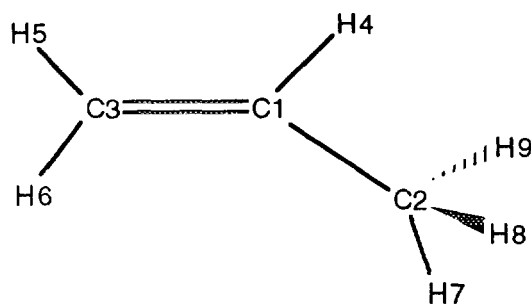


FIG. 1. Labeling used for the atoms in propene.

TABLE IV
Reference Geometry of Propene^{a,b}

C ₁ C ₂	1.5008	H ₅ C ₁ C ₃	121.880
C ₁ C ₃	1.3361	H ₆ C ₁ C ₃	121.932
C ₃ C ₁ C ₂	124.822	H ₄ C ₁ C ₂	115.559
C ₁ H ₄	1.0811	H ₇ C ₂ C ₁	111.109
C ₃ H ₅	1.0778	H ₈ C ₂ C ₁	110.731
C ₃ H ₆	1.0790	H ₇ C ₂ H ₈	108.386
C ₂ H ₇	1.0871	H ₈ C ₂ H ₉	107.372
C ₂ H ₈	1.0900	H ₇ C ₂ C ₁ C ₃	0.000
C ₂ H ₉	1.0900	H ₈ C ₂ C ₁ C ₃	120.507

a) see text for the determination of this geometry.

b) distances are given in Å and angles in degrees.

TABLE V
Computed and Observed Fundamental Wave
Numbers (cm⁻¹) of Propene

ν_i	4-21G RHF ^a	expt. ^b	Characterization ^c
21	199 (0.45)	188	96 q ₂₁
20	563 (12.5)	575	50 q ₂₀ + 33 q ₁₉
19	928 (55.7)	912	99 q ₁₈
18	997 (8.6)	990	67 q ₁₉ + 23 q ₂₀
17	1050 (0.02)	1045	71 q ₁₇
16	1443 (6.8)	1442	93 q ₁₅
15	2959 (32.1)	2953	50 q ₇ + 50 q ₈
14	413 (0.94)	428	85 q ₉
13	915 (1.3)	919	68 q ₁
12	932 (4.2)	934	49 q ₁₆ + 36 q ₁₂
11	1175 (0.62)	1174	31 q ₁₆ + 28 q ₁₂
10	1298 (0.16)	1298	62 q ₁₀
9	1381 (2.7)	1378	95 q ₁₃
8	1429 (0.67)	1414	47 q ₁₁ + 32 q ₁₄
7	1458 (9.1)	1458	61 q ₁₄ + 28 q ₁₁
6	1647 (7.4)	1653	65 q ₂
5	2916 (26.7)	2932	41 q ₇ + 41 q ₈
4	2988 (13.7)	2973	78 q ₆
3	3024 (23.3)	2991	37 q ₃ + 32 q ₄ + 28 q ₅
2	3036 (7.7)	3014	55 q ₃ + 33 q ₅
1	3101 (25.5)	3091	59 q ₄ + 38 q ₅

a) Present work; intensities (km. mol⁻¹) in parentheses.

b) Ref.(38).

c) Coordinates dominant according to the M-matrix criterion (39,40) are indicated by their internal coordinate number defined in Table III.

TABLE VI

Scaled Quantum Mechanical Force Field for Propene (Units Are Consistent with Energy in aJ, Distances in Å, and Angles in rad)

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21
1	4.7104																				
2	0.1669	8.8410																			
3	0.0741	0.0831	5.0470																		
4	-0.0045	0.0624	0.0173	5.1795																	
5	0.0134	0.0727	-0.0017	0.0355	5.1397																
6	0.0536	0.0182	-0.0087	-0.0035	0.0130	4.8946															
7	0.1018	-0.0095	0.0121	0.0043	-0.0017	0.0433	4.7942														
8	0.1018	-0.0095	0.0121	0.0043	-0.0017	0.0433	0.0580	4.7942													
9	0.2376	0.1606	-0.1548	0.0508	-0.0558	-0.0616	0.0308	0.0308	1.0448												
10	0.1784	-0.1973	-0.0083	0.0075	-0.0266	0.0216	0.0017	0.0017	0.0080	0.5208											
11	-0.0017	-0.2164	-0.0092	0.0616	0.0608	-0.0067	-0.0008	-0.0008	-0.0152	0.0152	0.4520										
12	-0.0429	-0.0008	0.0350	-0.1049	0.1107	0.0050	-0.0050	-0.0050	-0.0784	-0.0400	0.0000	0.5280									
13	-0.3372	-0.0090	-0.0138	-0.0024	-0.0081	0.0708	0.0676	0.0676	-0.0336	-0.0133	0.0047	0.0055	0.5531								
14	-0.0352	0.0041	-0.0008	-0.0033	0.0024	-0.1205	0.0700	0.0700	-0.0117	0.0000	-0.0008	0.0008	0.0054	0.5462							
15	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.1083	-0.1083	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.5393						
16	0.0285	-0.0374	0.0269	-0.0114	0.0114	0.0969	-0.0537	-0.0537	-0.1189	0.0649	0.0023	0.0102	-0.0038	-0.0092	0.0000	0.6418					
17	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0969	-0.0969	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0107	0.0000	0.6120				
18	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0008	0.0008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0015	0.0000	-0.0149	0.2475			
19	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0090	0.0090	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0054	0.0000	-0.0393	0.0008	0.1296		
20	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0087	0.0087	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0037	0.0000	-0.0538	0.0321	-0.0008	0.2562	
21	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	-0.0074	0.0074	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0035	0.0000	0.0017	-0.0009	0.0053	0.0051	0.0100

TABLE VII

Computed and Experimental Centrifugal Distortion Constants (in kHz)

	exp.	calc.	diff (%) ^a	calc* ^b	diff*(%)
Δ_j	6.2596 (19)	6.561	-4.82	6.561	-4.82
Δ_{jk}	-40.032 (21)	-34.578	13.62	-46.781	-16.86
Δ_k	465.53 (10)	510.791	-9.72	522.94	-12.33
δ_j	1.2284 (3)	1.28	-4.20	1.28	-4.20
δ_k	16.093 (30)	-22.921	242.43	15.931	1.01
T_{xx}	-8.716 (20)	-9.120	-4.63	-9.12	-4.63
T_{yy}	-3.803 (20)	-4.002	-5.23	-4.002	-5.24
T_{zz}	-431.758 (106)	-482.725	-11.80	-482.73	-11.81
T_1	21.253 (26)	14.885	29.96	27.10	-27.51
T_2	-0.461 (4)	-2.222	-381.62	-0.086	81.36

a) diff represents the ratio (exp - calc) / exp, in percent unit.

b) calculated values with $F_{21} = 100$ aJ.

torsion motion, for the reasons mentioned in our previous work on acetone (24). The scaled quantum mechanical (SQM) (21) force field given in Table VI was used in the calculation of the quartic centrifugal distortion constants. The experimental and calculated centrifugal distortion constants are compared in Table VII.

SPECTRUM ANALYSIS

Identification of the MW lines was quite straightforward, as earlier studies (1, 5) provided useful predictions about approximate frequencies and A - E splittings. Due to the high barrier these splittings are small. In the microwave region some forbidden transitions have also been observed and are reported in Table I. A least-squares program based on the internal axis method (IAM) was used to calculate the molecular parameters from the observed transitions and splittings. This program is similar to the program reported in Ref. (25), but it allows refinement of the sextic centrifugal distortion constants (26-28). Equal weights were given to the A - and E -type lines. The resulting parameters are given in Table II, together with their standard deviation and their correlation coefficients. All the parameters are well determined, including I_a , which is determined for the first time (it was constrained to a calculated value in previous studies). It has the expected order of magnitude. The standard deviation is 60 kHz

TABLE VIII

Experimental and Calculated Potential Barriers V_3 (cm^{-1})

Value	Method	Ref.
686.7	MW	(5)
684.75 (10)	MW	this work
693.7	FIR	(12)
646.4	ab initio, DZ RHF	(12)
724.1	ab initio, 6-31G (d,p) RHF	(13)
693.0	ab initio, 6-31G (d,p) MP2	(13)

for the *A*-type and 78 kHz for the *E*-type lines, which is of the same order of magnitude as the experimental accuracy. In Table VIII, we compare the value of the potential barrier V_3 to the previous experimental values and to recent ab initio values.

The *A* lines were also fitted to a Watson's Hamiltonian (*A* reduction, I' representation) because the effective molecular parameters determined in this way are useful for a straightforward prediction of the *A*-type spectrum. The standard deviation of the fit was 165 kHz. The parameters derived from the fit are listed in Table II.

The splittings were also fitted using Woods' program (29). The values of I_α , V_3 , and θ derived by this method are compatible, within three standard deviations, with the values obtained in our global fit. This agreement is expected as the approximations made by Woods in his treatment of the IAM theory are suitable in our case due to the fact that the potential barrier is high.

CENTRIFUGAL DISTORTION CONSTANTS

The frequencies computed from the SQM 4-21G RHF quadratic force field agree with their experimental counterparts with a mean deviation of only 10.9 cm^{-1} . This suggests that the force field calculated a priori for propene is of high quality and it should provide theoretical quartic centrifugal distortion constants of considerable accuracy (24, 30–35).

For the Δ constants the agreement is indeed rather good except for δ_K , which is calculated with the wrong sign. This is due to the fact that the internal rotation motion was directly included in the rotational Hamiltonian used to determine the experimental constants. To allow a meaningful comparison, the torsional force constant should not be included in the calculation of the centrifugal distortion constants. We have calculated the theoretical distortion constants without taking into account the torsional constant (naturally, Δ_J and δ_J do not change as they are insensitive to the value of the torsional force constant). The resulting agreement is very good, as can be seen in Table VII. Similar agreement was obtained for acetone-d1 (24). If one considers the determinable parameters T , as defined by Watson (36), the agreement between theory and experiment is good for the parameters T_{aa} , which do not depend on the torsional motion. On the other hand, there are larger deviations for T_1 and T_2 , which do depend on the torsion. T_2 is particularly poorly reproduced. This could partly be explained by the fact that the torsional frequency is rather high, so probably it cannot be isolated from the other vibrational frequencies. Finally, it should be noted that accurate experimental determination of T_2 is known to be difficult.

ACKNOWLEDGMENTS

The theoretical part of the research, performed in Budapest, Hungary, was partially supported by grants from the Scientific Research Foundation of Hungary (OTKA 2101 and FO13962). G.W. and J.D. thank the A.T.P. "Planétologie" (CNRS) for financial support.

Note added in proof: A study of the millimeter and submillimeterwave spectrum of propene by De Lucia and coworkers has been recently published (*J. Mol. Spectrosc.* **166**, 120–129 (1994)). This paper contains complementary data to ours and a different model for the analysis of the spectrum. Our conclusions are in good agreement with this paper.

RECEIVED: May 18, 1994

REFERENCES

1. D. R. LIDE AND D. E. MANN, *J. Chem. Phys.* **27**, 868-873 (1957).
2. D. R. HERSCHBACH AND L. C. KRISHER, *J. Chem. Phys.* **28**, 728-729 (1958).
3. D. R. LIDE AND D. CHRISTENSEN, *J. Chem. Phys.* **35**, 1374-1378 (1961).
4. E. HIROTA AND Y. MORINO, *J. Chem. Phys.* **45**, 2326-2327 (1966).
5. E. HIROTA, *J. Chem. Phys.* **45**, 1984-1990 (1966).
6. E. HIROTA, T. HIROOKA, AND Y. MORINO, *J. Mol. Spectrosc.* **26**, 351-367 (1968).
7. E. HIROTA, *J. Mol. Spectrosc.* **34**, 516-527 (1970).
8. W. G. FATELEY AND F. A. MILLER, *Spectrochim. Acta* **19**, 611-628 (1963).
9. K. D. MÖLLER, A. R. DEMEO, R. D. SMITH, AND L. H. LONDON, *J. Chem. Phys.* **47**, 2609-2616 (1967).
10. C. E. SOUTER AND J. L. WOOD, *J. Chem. Phys.* **52**, 674-682 (1970).
11. E. C. TUAZON, A. S. MANOCHA, AND W. G. FATELEY, *Chem. Phys. Lett.* **23**, 63-68 (1973).
12. J. R. DURIG, G. A. GUIRGIS, AND S. BELL, *J. Phys. Chem.* **93**, 3487-3491 (1989).
13. L. GOODMAN AND A. G. OZKABAK, *J. Mol. Struct. (Theochem.)* **261**, 367-384 (1992).
14. R. L. BENSON AND W. H. FLYGARE, *Chem. Phys. Lett.* **4**, 141-143 (1969).
15. H. S. TAM, J.-I. CHOE, AND M. D. HARMONY, *J. Phys. Chem.* **95**, 9267-9272 (1991).
16. J. BURIE, D. BOUCHER, J. DEMAISON, AND A. DUBRULLE, *J. Phys. (Orsay)* **43**, 1319-1325 (1982).
17. H. DREIZLER, *Mol. Phys.* **59**, 1-28 (1986).
18. P. PULAY, G. FOGARASI, F. PANG, AND J. E. BOGGS, *J. Am. Chem. Soc.* **101**, 2550-2560 (1979).
19. G. FOGARASI, X. ZHOU, P. W. TAYLOR, AND P. PULAY, *J. Am. Chem. Soc.* **114**, 8191-8201 (1992).
20. P. BOWERS AND L. SCHÄFER, *J. Mol. Struct.* **69**, 233-240 (1980).
21. P. PULAY, G. FOGARASI, G. PONGOR, J. E. BOGGS, AND A. VARGHA, *J. Am. Chem. Soc.* **105**, 7037-7047 (1983).
22. W. D. ALLEN, A. G. CSÁSZÁR, AND D. A. HORNER, *J. Am. Chem. Soc.* **114**, 6834-6849 (1992).
23. C. E. BLOM AND C. ALTONA, *Mol. Phys.* **33**, 875-885 (1977).
24. G. WLODARCZAK, J. DEMAISON, B. P. VAN EIJCK, M. ZHAO, AND J. E. BOGGS, *J. Chem. Phys.* **94**, 6698-6707 (1991).
25. B. P. VAN EIJCK, J. VAN OPHEUSDEN, M. M. M. VAN SHAIK, AND E. VAN ZOEREN, *J. Mol. Spectrosc.* **86**, 465-479 (1981).
26. H. MAES, B. P. VAN EIJCK, A. DUBRULLE, AND J. DEMAISON, *Z. Naturforsch.* **41a**, 743-746 (1986).
27. H. MAES, G. WLODARCZAK, D. BOUCHER, AND J. DEMAISON, *Z. Naturforsch.* **42a**, 97-102 (1986).
28. J. DEMAISON, H. MAES, B. P. VAN EIJCK, G. WLODARCZAK, AND M. C. LASNE, *J. Mol. Spectrosc.* **125**, 214-224 (1987).
29. R. C. WOODS, *J. Mol. Spectrosc.* **21**, 4-24 (1966).
30. A. G. CSÁSZÁR AND G. FOGARASI, *J. Chem. Phys.* **89**, 7646-7648 (1988).
31. G. WLODARCZAK, J. BURIE, J. DEMAISON, K. VORMANN, AND A. G. CSÁSZÁR, *J. Mol. Spectrosc.* **134**, 297-304 (1989).
32. A. G. CSÁSZÁR, G. FOGARASI, AND J. E. BOGGS, *J. Phys. Chem.* **93**, 7644-7651 (1989).
33. A. G. CSÁSZÁR, *Chem. Phys. Lett.* **162**, 361-368 (1989).
34. D. A. CLABO, JR., W. D. ALLEN, R. B. REMINGTON, Y. YAMAGUCHI, AND H. F. SCHAEFER III, *Chem. Phys.* **123**, 187-239 (1988).
35. W. D. ALLEN, Y. YAMAGUCHI, A. G. CSÁSZÁR, D. A. CLABO, JR., R. B. REMINGTON, AND H. F. SCHAEFER III, *Chem. Phys.* **145**, 427-466 (1990).
36. J. K. G. WATSON, in "Vibrational Spectra and Structure" (J. R. Durig, Ed.), Vol. 6, Elsevier, Amsterdam, 1977.
37. Y. XIE AND J. E. BOGGS, *J. Comput. Chem.* **7**, 158-164 (1986).
38. B. SILVI, P. LABARBE, AND J. P. PERCHARD, *Spectrochim. Acta* **29A**, 263-271 (1973).
39. P. PULAY AND F. TÖRÖK, *Acta. Chim. Hung.* **44**, 287-292 (1965).
40. G. KERESZTURY AND G. JALSOVSKY, *J. Mol. Struct.* **10**, 304-305 (1971).