

The Millimeter-Wave and Submillimeter-Wave Spectrum of Propylene (CH₃CHCH₂)

J. C. PEARSON,* K. V. L. N. SASTRY,† ERIC HERBST,* ‡
AND FRANK C. DE LUCIA*

Departments of * Physics and ‡ Astronomy, The Ohio State University, Columbus, Ohio 43210; and
† Department of Physics, University of New Brunswick, Fredericton, New Brunswick, E3B 5A3 Canada

The rotational-torsional spectrum of the internal rotor propylene (CH₃CHCH₂) has been extended into the millimeter-wave and submillimeter-wave regions of the electromagnetic spectrum. Approximately 760 lines belonging to the *A* and *E* torsional substates of the ground ($v_t = 0$) torsional state have been measured through rotational quantum number $J = 30$ and up to a frequency of 412 GHz. These lines have been added to approximately 40 previously measured rotational transitions in the microwave region to make up a data set which has been fit to 90 kHz using our internal axis method. The threefold potential barrier for torsional motion that we determine agrees well with previous values. The spectra reported here should be useful for interstellar searches for propylene, which should be directed toward high-mass star-forming regions, where the degree of saturation is higher than in quiescent sources. © 1994 Academic Press, Inc.

I. INTRODUCTION

Propylene (CH₃CHCH₂) is an internal rotor with a moderately high potential barrier against the torsional motion of the methyl group. The rotational-torsional spectrum of this molecule in the microwave region was studied by several groups in the 1950s and 1960s although no additional laboratory work has been undertaken since that time to the best of our knowledge. In 1957, Lide and Mann (1) reported the frequencies of 14 spectral lines in the region 17–36 GHz belonging to the ground torsional state ($v_t = 0$) of normal propylene and its isotopomer H₃CC¹³HCH₂ in their *A* and *E* torsional substates. The *A*-species lines were fit to a semirigid rotor model and the small spectral splittings between the *A* and *E* lines were utilized to determine a threefold potential barrier for torsion of $692.4 \pm 6 \text{ cm}^{-1}$. The components of the dipole moment were found to be $\mu_a = 0.360 \pm 0.001 \text{ D}$ and $\mu_b = 0.05 \pm 0.02 \text{ D}$ via Stark effect measurements. The structure of propylene was obtained by Lide and Christensen several years later (2) via microwave studies of seven isotopic species. Hirota (3) later studied the microwave spectrum of the first three torsional states of propylene ($v_t = 0, 1, 2$) and fit the data using the principal axis method (PAM). He determined the threefold potential barrier V_3 to be $698.4 \pm 0.5 \text{ cm}^{-1}$ and the sixfold barrier V_6 to be $-13 \pm 2 \text{ cm}^{-1}$. Lovas and Suenram (4) later tabulated and reanalyzed the data.

Propylene is a reasonable candidate for interstellar detection despite its relatively small dipole moment. Molecular detections in interstellar space are typically made in the millimeter-wave region of the spectrum, however, and millimeter-wave spectral data for propylene do not exist. Several hydrocarbons with three carbon atoms have already been detected in interstellar space and/or the carbon-rich circumstellar envelope IRC+10216. These include C₃ (5), both cyclic and noncyclic forms of C₃H and C₃H₂ (6–9), and methyl acetylene (C₃H₄) (10). Propylene is of course more

TABLE I—Continued

J'	K _a '	K _c '	J''	K _a ''	K _c ''	Frequency (MHz)	Residual (MHz)	E _U (cm ⁻¹)	E _L (cm ⁻¹)	μ ² S
23	20	3	22	20	2	401522.865	-0.095	659.442	646.049	0.712
23	20	4	22	20	3	401522.865	-0.095	659.442	646.049	0.712
23	21	2	22	21	1	401556.910	-0.251	710.298	696.904	0.486
23	21	3	22	21	2	401556.910	-0.251	710.298	696.904	0.486
23	10	13	22	10	12	401582.893	-0.068	285.825	272.429	2.370
23	10	14	22	10	13	401582.893	-0.068	285.825	272.429	2.370
23	9	14	22	9	13	401690.284	-0.053	262.093	248.694	2.450
23	9	15	22	9	14	401690.284	-0.053	262.093	248.694	2.450
23	8	15	22	8	14	401854.491	0.012	240.864	227.460	2.570
23	8	16	22	8	15	401854.491	0.020	240.864	227.460	2.570
23	7	17	22	7	16	402110.790	0.177	222.149	208.736	2.653
23	7	16	22	7	15	402110.790	-0.179	222.149	208.736	2.653
23	6	18	22	6	17	402524.154	-0.031	205.963	192.536	2.725
23	6	17	22	6	16	402535.451	0.034	205.964	192.537	2.725
30	6	25	30	5	26	402897.473	0.014	316.433	302.994	0.048
23	5	19	22	5	18	403161.826	-0.012	192.332	178.884	2.785
23	5	18	22	5	17	403390.970	0.005	192.354	178.898	2.785
23	4	20	22	4	19	403516.473	-0.027	181.222	167.763	2.835
29	6	24	29	5	25	403764.988	-0.128	298.882	285.414	0.046
26	6	20	26	5	21	404376.365	0.027	249.775	236.287	0.040
28	6	23	28	5	24	404650.204	-0.086	281.922	268.424	0.044
27	6	22	27	5	23	405528.940	0.011	265.552	252.025	0.042
25	6	19	25	5	20	405807.401	0.023	234.583	221.046	0.038
23	4	19	22	4	18	406121.922	-0.032	181.534	167.987	2.835
26	6	21	26	5	22	406381.677	0.008	249.771	236.216	0.040
24	6	18	24	5	19	407012.743	0.060	219.979	206.403	0.036
25	6	20	25	5	21	407193.515	-0.047	234.580	220.998	0.038
24	6	19	24	5	20	407953.701	0.008	219.978	206.370	0.036
23	6	18	23	5	19	408654.647	-0.073	205.963	192.332	0.035
22	6	16	22	5	17	408883.587	-0.074	192.537	178.898	0.033
22	6	17	22	5	18	409292.338	-0.034	192.536	178.884	0.033
24	2	23	23	2	22	409297.461	-0.005	177.420	163.768	3.021
23	2	22	22	1	21	409609.525	0.147	163.768	150.104	0.038
21	6	16	21	5	17	409864.910	-0.031	179.697	166.025	0.031
20	6	14	20	5	15	410210.469	-0.011	167.444	153.761	0.029
23	2	21	22	2	20	410218.928	-0.008	169.341	155.658	2.896
19	6	13	19	5	14	410719.313	-0.151	155.778	142.078	0.027
19	6	14	19	5	15	410817.808	-0.050	155.778	142.074	0.027
18	6	12	18	5	13	411145.395	0.000	144.697	130.983	0.026
18	6	13	18	5	14	411203.314	-0.008	144.697	130.981	0.026
17	6	11	17	5	12	411500.144	-0.010	134.202	120.476	0.024
17	6	12	17	5	13	411533.195	0.031	134.202	120.475	0.024
16	6	10	16	5	11	411793.719	-0.054	124.292	110.556	0.022
16	6	11	16	5	12	411811.992	0.082	124.292	110.555	0.022
24	1	23	23	1	22	411935.180	0.009	177.052	163.312	3.024

K) era, and then evaporated into the gas phase when temperatures rose to their current values ($T \approx 100\text{--}200$ K) (12).

In this paper, we report the extension of the rotational-torsional spectrum of propylene in its ground torsional state into the millimeter-wave and submillimeter-wave regions. Our data should prove useful to radio astronomers interested in searching for this species.

II. EXPERIMENT AND THEORY

The sample of CH₃CHCH₂ was purchased from Aldrich Chemicals and directed into an absorption cell of length 2 m at room temperature and at a pressure of 50 mTorr. We utilized our klystron-based spectrometer, in which harmonic generation from 40- to 60-GHz klystrons is employed to produce millimeter-wave and submillimeter-wave radiation (13). The absorption spectrum was detected with a 1.8 K InSb hot electron bolometer or a 0.32 K Si bolometer, and the frequency-modulated second-derivative spectra were digitized on a Macintosh computer. Lines have been measured through 412 GHz in frequency. Despite the small size of the component of the dipole moment along the *b* principal axis, many *b*-type ($\Delta K_a = \pm 1$) spectral lines were measured without undue difficulty. A total of 420 *A*-state and 383 *E*-state lines were resolved well enough to include in the analysis. The estimated measurement accuracy is better than 100 kHz except for blended lines and the weakest *b*-type transitions. The blending problem exists, especially for *a*-type ($\Delta K_a = 0$) transitions, since the

TABLE II—Continued

J'	K _a '	K _c '	J''	K _a ''	K _c ''	Frequency (MHz)	Residual (MHz)	E _J (cm ⁻¹)	E _L (cm ⁻¹)	μ _{2S}
23	13	10	22	13	9	401437.838	0.003	371.974	358.584	1.989
23	17	6	22	17	5	401448.771	-0.174	521.501	508.110	1.326
23	17	7	22	17	6	401450.099	0.241	521.501	508.110	1.326
23	19	5	22	19	4	401496.113	-0.034	611.016	597.624	0.928
23	11	12	22	11	11	401509.285	-0.020	312.055	298.662	2.254
23	11	13	22	11	12	401510.832	0.052	312.055	298.662	2.254
23	20	3	22	20	2	401521.698	0.168	659.444	646.050	0.712
23	21	2	22	21	1	401553.901	0.013	710.302	696.907	0.486
23	21	3	22	21	2	401557.988	0.275	710.299	696.904	0.486
23	10	13	22	10	12	401579.979	0.021	285.827	272.432	2.370
23	10	14	22	10	13	401582.893	0.059	285.826	272.430	2.370
23	22	1	22	22	0	401589.814	-0.216	763.586	750.190	0.249
23	9	14	22	9	13	401688.638	0.009	262.095	248.696	2.476
23	9	15	22	9	14	401691.970	-0.079	262.092	248.693	2.476
23	8	15	22	8	14	401854.491	-0.120	240.865	227.461	2.570
23	8	16	22	8	15	401857.410	-0.139	240.863	227.458	2.570
23	7	16	22	7	15	402112.781	-0.031	222.148	208.735	2.653
23	7	17	22	7	16	402114.308	-0.042	222.146	208.733	2.653
23	6	18	22	6	17	402528.585	-0.039	205.961	192.534	2.683
23	6	17	22	6	16	402537.407	-0.007	205.962	192.535	2.683
27	6	21	27	5	22	402676.467	0.133	265.556	252.124	0.042
30	6	25	30	5	26	402899.545	0.036	316.431	302.992	0.048
23	5	19	22	5	18	403164.689	-0.039	192.330	178.882	2.785
23	5	18	22	5	17	403393.581	-0.024	192.352	178.896	2.785
23	4	20	22	4	19	403517.814	0.025	181.221	167.761	2.835
29	6	24	29	5	25	403766.126	0.101	298.881	285.412	0.046
26	6	20	26	5	21	404375.287	0.088	249.774	236.285	0.040
28	6	23	28	5	24	404650.204	0.083	281.920	268.423	0.044
12	3	9	11	2	10	404674.683	0.045	56.807	43.309	0.010
27	6	22	27	5	23	405527.695	-0.028	265.550	252.023	0.042
25	6	19	25	5	20	405806.024	-0.066	234.581	221.045	0.038
23	4	19	22	4	18	406123.754	-0.031	181.533	167.986	2.835
24	6	18	24	5	19	407011.581	0.095	219.977	206.401	0.035
24	6	19	24	5	20	407949.269	0.096	219.976	206.368	0.035
23	6	18	23	5	19	408648.874	0.063	205.961	192.330	0.031
22	6	16	22	5	17	408883.587	0.094	192.535	178.896	0.027
22	6	17	22	5	18	409284.689	-0.226	192.534	178.882	0.027
24	2	23	23	2	22	409295.174	-0.011	177.421	163.768	3.021
23	2	22	22	1	21	409597.409	-0.082	163.768	154.607	0.038
21	6	16	21	5	17	409856.123	0.104	179.694	166.023	0.021
23	2	21	22	2	20	410215.024	-0.003	169.342	155.659	2.896
20	6	15	20	5	16	410363.006	0.127	167.441	153.753	0.016
19	6	13	19	5	14	410719.313	-0.340	155.775	142.075	0.012
17	6	12	17	5	12	411478.707	0.184	134.199	120.473	0.020
16	6	11	16	5	11	411768.581	0.192	124.289	110.554	0.021
24	1	23	23	1	22	411931.299	-0.007	177.053	163.313	3.024

axis system to lowest order, we must consider such coupling between the torsional angular momentum and the rigid body angular momentum in the a direction. The Coriolis coupling reasserts itself in the internal system in the form of peculiar boundary conditions on the rotational-torsional wavefunctions, so that little is gained in practice by using the proper internal axes. The direction of the a (prolate) axis, defined to minimize coupling between the torsional angular momentum and the rigid body angular momentum along the b axis, here lies approximately 5° from the analogous a principal axis, so that the a dipole component μ_a is virtually indistinguishable from that measured in the principal axis system (I). The small size of μ_b in the principal axis system leads to a large relative uncertainty in μ_b when projected into our axis system, and this large relative uncertainty affects the calculated intensities severely, since they are very small. A best value for the rotated μ_b was determined by comparing the calculated intensities in our IAM program both with measured intensities and with intensities for the A torsional substate determined with an asymmetric rotor program.

The IAM program has been modified for the study of propylene so that the energy levels in both the A and E torsional substates are characterized by asymmetric top (J , K_a , K_c) quantum numbers rather than the symmetric top/parity designations used for methanol. This modification is reasonable for propylene in both A and E substates because splittings due to internal rotation are small due to the large height of the

potential barrier. A global fit to data in the *A* and *E* states has been utilized rather than the separate fits needed for methanol. The predictions of our program for both *a*-type and *b*-type spectra based on a fit to the original microwave data were sufficiently good to allow rapid assignment of many lines at higher frequencies and rotational quantum numbers by the usual bootstrap procedure.

III. ANALYSIS AND DISCUSSION

A total of 803 rotational transitions (420 *A* and 383 *E*) in the $v_t = 0$ state of propylene involving rotational quantum numbers up to $J = 30$ and $K_a = 22$ have been analyzed and fit with our IAM approach to a root-mean-square deviation of 90 kHz by varying 14 parameters. Except for the small number (≈ 40) of previously reported $v_t = 0$ transitions, the spectral lines are all reported for the first time. All previously measured lines have been included in the fit with the exception of the $6_{2,4}-7_{1,7}$ transition at 9409 MHz, which we have not been able to fit to reasonable accuracy. The analyzed transitions are listed in Tables I (*A* torsional substate) and II (*E* torsional substate). In addition to the quantum assignments and measured frequencies, the tables contain residuals (observed-calculated frequencies), upper and lower state wavenumbers with respect to the lowest energy level, and intensities. The intensities are listed as the square of the relevant dipole moment component multiplied by the *S* value (20). Note that the intensities of the *b*-type ($\Delta K_a = \pm 1$) lines are very low and uncertain because of the small, uncertain value of the dipole moment in the *b* direction. Astronomical searches should therefore be directed toward the *a*-type ($\Delta K_a = 0$) lines. The small *A/E* splittings, if resolvable, and dense bandheads should provide clues to the carrier of the lines.

To fit the lines in Tables I and II required variation of only the four rotational constants *A*, *B*, *C*, D_{ab} ; the complete set of five fourth-order distortion constants Δ_{JK} , Δ_J , Δ_K , δ_J , δ_K ; three sixth-order distortion constants; the threefold potential barrier V_3 ; and the unitless torsional parameter ρ . Two other constants— V_6 and *F*—were fixed at previously determined values. The parameter *F*, which is the rotational constant for internal rotation, was fixed at a value determined by the molecular structure (1-3), while the sixfold potential barrier was fixed at the value determined by Hirota (3). Both of these constants can only be determined if spectra from more than one torsional state are included in the fit. It should be noted that D_{ab} is in principle determinable from a combination of other internal rotation parameters. As a result of the fairly rigid nature of propylene, D_{ab} is highly correlated with the rotational constants, as expected. We chose to fit for D_{ab} in our analysis rather than to leave it fixed and drive the uncertainty in the rotational constants down artificially. The small number of required parameters is in sharp contrast with the case of methanol where a very large number of so-called interaction constants is required (14-17). Methanol possesses a much lower barrier against torsional motion and a much higher value of ρ , the parameter which determines the size of the lowest order coupling between torsional and end-over-end angular momentum along the *a* axis.

The constants determined in this work are reported in Table III with 1σ deviations. Only some of the reported constants can be compared with previous work because of the differing axis systems used and our inclusion of sixth-order centrifugal distortion. Perhaps the most significant constant to be compared is V_3 . Our threefold potential barrier of 697.5 cm^{-1} is within $1-2\text{ cm}^{-1}$ of the previously determined value by Hirota (3). The values of 692.4 cm^{-1} by Lide and Mann (1) and 687.9 cm^{-1} by Lovas and

TABLE III
Spectroscopic Constants for Propylene^a

Constant	Value (MHz unless noted)	Uncertainty (1 σ)
A	45954.88817	(37000)
B	9634.600366	(370000)
C	8130.239286	(1100)
D _{ab}	-3457.68165	(1.90000)
F (cm ⁻¹)	7.1007	(fixed) ^b
ρ (unitless)	0.2635849	(370)
V ₃ (cm ⁻¹)	697.4987	(480)
$\Delta_{JK} \times 10^3$	-53.20356	(3000)
$\Delta_J \times 10^3$	6.448711	(570)
$\Delta_K \times 10^3$	487.36038	(7300)
$\delta_J \times 10^3$	1.311460	(620)
$\delta_K \times 10^3$	7.34341	(680)
V ₆ (cm ⁻¹)	-13.0	(fixed) ^c
H _{JK} \times 10^8}	9.08969	(54000)
H _{KJ} \times 10^8}	-313.298	(720)
h _{J} \times 10^9}	1.835	(470)

^a The number of significant figures for each constant is necessary to reproduce the calculated frequencies to 10 kHz. The uncertainty is given to two significant figures.

^b Based on structure of Ref. (2). See Ref. (3).

^c Determined in Ref. (3).

Suenram (4) are also reasonably close, considering that these authors did not include a V_6 correction.

In addition to the lines reported in Tables I and II, the parameters we have determined allow us to predict the frequencies and associated uncertainties of many lines with $J \leq 30$ not measured in the laboratory. These predictions, which have been made through 500 GHz, are available upon request.

ACKNOWLEDGMENTS

We acknowledge the support of the National Aeronautics and Space Administration for our program in laboratory astrophysics. We also thank the Ohio Supercomputer Center for time on their Cray Y-MP 8 computer.

RECEIVED: February 10, 1994

REFERENCES

1. D. R. LIDE, JR., AND D. E. MANN, *J. Chem. Phys.* **27**, 868-873 (1957).
2. D. R. LIDE, JR., AND D. CHRISTENSEN, *J. Chem. Phys.* **35**, 1374-1378 (1961).
3. E. HIROTA, *J. Chem. Phys.* **45**, 1984-1990 (1966).
4. F. J. LOVAS AND R. D. SUENRAM, *J. Phys. Chem. Ref. Data* **18**, 1245-1524 (1989).
5. K. H. HINKLE, J. J. KEADY, AND P. F. BERNATH, *Science* **241**, 1319-1322 (1988).
6. C. A. GOTTLIEB, J. M. VRTELEK, E. W. GOTTLIEB, P. THADDEUS, AND Å. HJALMARSON, *Astrophys. J.* **294**, L55-L58 (1985).
7. S. YAMAMOTO, S. SAITO, M. OHISHI, H. SUZUKI, S. ISHIKAWA, N. KAIFU, AND A. MURAKAMI, *Astrophys. J.* **322**, L55-L58 (1987).

8. P. THADDEUS, J. M. VRTILEK, AND C. A. GOTTLIEB, *Astrophys. J.* **299**, L63-L66 (1985).
9. J. CERNICARO, C. A. GOTTLIEB, M. GUELIN, T. C. KILLIAN, G. PAUBERT, P. THADDEUS, AND J. M. VRTILEK, *Astrophys. J.* **368**, L39-L41 (1991).
10. L. E. SNYDER AND D. BUHL, *Nature Phys. Sci.* **243**, 45-46 (1973).
11. G. A. BLAKE, E. C. SUTTON, C. R. MASSON, AND T. G. PHILLIPS, *Astrophys. J.* **315**, 621-645 (1987).
12. P. CASELLI, T. I. HASEGAWA, AND E. HERBST, *Astrophys. J.* **408**, 548-558 (1993).
13. P. HELMINGER, J. K. MESSER, AND F. C. DE LUCIA, *Appl. Phys. Lett.* **42**, 309 (1983).
14. E. HERBST, J. K. MESSER, F. C. DE LUCIA, AND P. HELMINGER, *J. Mol. Spectrosc.* **108**, 42-57 (1984).
15. F. C. DE LUCIA, E. HERBST, T. ANDERSON, AND P. HELMINGER, *J. Mol. Spectrosc.* **134**, 395-411 (1989).
16. T. ANDERSON, F. C. DE LUCIA, AND E. HERBST, *Astrophys. J. Suppl. Ser.* **82**, 405-444 (1992).
17. T. ANDERSON, E. HERBST, AND F. C. DE LUCIA, *J. Mol. Spectrosc.* **159**, 410-421 (1993).
18. W. LIANG, J. G. BAKER, E. HERBST, R. A. BOOKER, AND F. C. DE LUCIA, *J. Mol. Spectrosc.* **120**, 298-310 (1986).
19. M. LIU AND C. R. QUADE, *J. Mol. Spectrosc.* **146**, 238-251 (1991).
20. C. H. TOWNES AND A. L. SCHAWLOW, "Microwave Spectroscopy," Dover, New York, 1975.