The Millimeter- and Submillimeter-Wave Spectra of Acetaldehyde: Centrifugal Distortion and Internal Rotation Analysis

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Z. Naturforsch. **42a**, 97–102 (1987); received August 4, 1986

141 internal rotation doublets (282 transitions, among which 174 new measurements) of acetaldehyde in its ground torsional state have been measured up to 600 GHz ($J \leqq 32$). An overall fit of the measurements (including the lines identified by previous workers) using the Internal Axis Method has allowed us to accurately determine the rotational, centrifugal distortion and internal rotation constants. The quality of the fit is good enough to permit the accurate prediction of transition frequencies of possible astrophysical interest.

Introduction

Acetaldehyde (CH_3CHO) is a molecule of astrophysical interest. It has been first detected in Sgr B_2 from centimeter-wave observations [1]. This detection was confirmed many times, both in Sgr B_2 [2–4] and in Ori A [5]. In fact acetaldehyde seems to be relatively abundant in interstellar space, and it is a light molecule with strong transitions. So it promises to be an important tool for probing non-equilibrium population distribution processes, and many more of its transitions could be detected at millimeter and submillimeter wavelengths.

Since acetaldehyde is one of the simplest molecules with an internal degree of freedom, many ab initio SCF calculations have been made on this molecule [6]. Experimentally the internal rotation of the methyl group has been very extensively studied by far infrared [7–9] and microwave [10–17] spectroscopy. The most complete microwave study was that of Bauder and Günthard [12] who analyzed the rotational spectrum in its ground state and in several torsionally excited states using three different models including one with structure relaxation. Parallely Bauder and coll. published an extensive review of the existing microwave data [13]. The electric dipole moment was recently remeasured with a good accuracy: $\mu_a = 2.537(4)$ D and $\mu_b = 1.062(5)$ D [14]. Its orientation could also be determined from the quadratic Stark effect thanks to the fact that this molecule is nonrigid [15]. A r_s structure was determined by Nösberger and coll. [16] and a r_z structure by Iijima and Tsuchiya [17].

However despite this body of work, only low J transitions have been assigned so far. It is due to the facts that the molecule is light ($A = 57$ GHz, $B = 10$ GHz and $C = 9$ GHz) and therefore most transitions are in the millimeter-wave range and that the potential is low (reduced barrier $s = 4\,V_3/9\,F = 23.5$), so the splittings are large and difficult to calculate. A large number of transitions of acetaldehyde still have to be observed in the laboratory or accurately predicted to make easier the identification of radioastronomical spectra.

For these reasons we have measured the millimeter wave spectra of acetaldehyde and carried out a complete centrifugal distortion and internal rotation analysis so that accurate measurements and predictions would be available for the radioastronomers.

Experimental

The sample of acetaldehyde was purchased commercially from Fluka AG (Buchs, Switzerland) and was used without further purification.

The transitions between 120 GHz and 300 GHz were measured with a computer-controlled spectrometer with superheterodyne detection. It can either be source-modulated and tuned over a wide range of fixed frequency steps while the phase-demodulated signal is being plotted or it can be operated as a video spectrometer over a small scan which is controlled by a signal averager which accumulates the signal and calculates the line fre-

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Table 1. Measured ground state transitions of acetaldehyde.

J	K_-	K_+	←	J	K_-	K_+	freq (A)	cal−obs	freq (E)	cal−obs
2	0	2		1	0	1	38 512.113	− 0.097	38 505.999	0.065
2	1	1		1	1	0	39 594.287	− 0.067	39 362.504	0.273
2	1	2		1	1	1	37 464.168	− 0.011	37 686.868	− 0.127
1	1	1		2	0	2	8 243.482	− 0.006	7 391.293	0.407
2	1	2		1	0	1	84 219.764	− 0.115	83.584.260	0.245
3	0	3		2	1	2	12 014.999	− 0.048	12 635.228	− 0.154
4	0	4		3	1	3	32 709.185	− 0.075	33 236.469	− 0.021
4	1	3		4	1	4	10 648.428	− 0.115	10 720.629	− 0.010
5	0	5		4	4	4	95 963.380	− 0.061	95 947.340	0.161
5	1	4		4	1	3	98 900.986	− 0.198	98 863.270	0.148
5	1	5		4	1	4	93 580.859	− 0.061	93 595.276	− 0.027
5	2	3		4	2	2	96 632.550	0.012	96 475.500	0.196
5	2	4		4	2	3	96 274.200	− 0.045	96 425.750	− 0.255
5	3	2		4	3	1	96 371.600	0.162	96 368.050	0.448
5	3	3		4	3	2	96 368.050	− 0.292	96 384.300	− 0.097
5	4	2		4	4	1	96 343.250	0.081	96 360.730	− 0.248
5	1	4		5	1	5	15 968.452	− 0.149	15 988.730	0.059
6	0	6		5	0	5	114 959.650	0.094	114 939.900	0.346
6	1	5		5	1	4	118 625.890	0.091	118 591.770	0.300
6	1	6		5	1	5	112 248.720	− 0.133	112 254.480	0.061
6	3	3		5	3	2	115 671.300	0.327	115 664.200	0.469
6	3	4		5	3	3	115 660.440	0.518	115 683.800	0.024
5	2	4		6	1	5	15 164.478	0.095	13 145.877	0.659
5	2	3		6	1	6	38 138.436	− 0.101	37 851.405	− 0.582
6	1	5		6	1	6	22 345.900	− 0.204	22 326.171	0.147
7	0	7		6	1	6	96 765.325	− 0.197	97 180.650	0.208
7	1	6		6	2	5	7 661.224	− 0.172	9 443.908	− 0.234
6	2	4		7	1	7	23 364.771	− 0.097	22 868.978	− 0.407
7	1	6		7	1	7	29 773.695	− 0.240	29 718.416	0.211
8	1	7		7	2	6	30 941.333	− 0.213	32 486.073	0.029
8	1	8		7	0	7	183 633.925	− 0.072	183 217.176	− 0.050
7	2	5		8	1	8	9 542.776	− 0.068	8 840.555	− 0.168
8	1	7		8	1	8	38 240.715	− 0.177	38 150.985	0.265
9	1	9		8	0	8	199 092.200	− 0.087	198 698.169	− 0.048
10	0	10		9	0	9	189 838.992	− 0.164	189 803.782	0.095
10	1	10		9	1	9	186 648.188	− 0.186	186 641.295	0.048
10	1	10		9	2	7	14 766.065	0.041	15 727.190	0.039
10	1	10		9	0	9	214 443.389	− 0.077	214 073.954	− 0.047
10	2	9		9	2	8	192 150.015	− 0.199	192 207.291	0.021
10	3	7		9	3	6	193 072.338	− 0.050	193 003.130	0.182
10	3	8		9	3	7	192 922.938	− 0.044	193 019.289	− 0.284
10	4	6		9	4	5	192 812.985	0.084	192 830.468	0.131
10	4	7		9	4	6	192 810.110	0.077	192 847.843	− 0.496
10	5	5		9	5	4	192 734.657	0.278	192 761.964	− 0.550
10	5	6		9	5	5	192 734.657	0.251	192 768.294	− 0.197
10	6	5		9	6	4	192 702.331	0.314	192 736.004	− 0.645
9	3	7		10	2	8	36 613.186	0.106	34 274.578	0.171
10	2	8		10	2	9	8 556.062	− 0.061	8 839.309	0.057
11	0	11		10	0	10	208 267.034	− 0.164	208 228.538	0.116
11	0	11		10	1	10	183 662.715	− 0.329	183 958.405	0.218
11	1	10		10	1	9	216 630.221	− 0.174	216 581.936	0.106
11	1	11		10	1	10	205 170.705	− 0.199	205 161.941	0.056
11	1	11		10	2	8	25 008.607	0.012	26 029.553	− 0.049
11	2	9		10	2	8	214 845.019	− 0.141	214 800.801	0.122

Table 1. (Continued).

J	K_-	K_+	←	J	K_-	K_+	freq (A)	cal−obs	freq (E)	cal−obs
11	3	8		10	3	7	212 498.631	− 0.043	212 400.951	0.220
11	3	9		10	3	8	212 257.119	− 0.039	212 384.722	− 0.256
11	4	7		10	4	6	212 134.154	0.097	212 151.898	0.123
11	4	8		10	4	7	212 128.397	0.102	212 171.475	− 0.448
11	5	7		10	5	6	212 029.196	0.237	212 066.053	− 0.155
11	5	6		10	5	5	212 029.196	0.305	212 059.551	− 0.544
11	6	6		10	6	5	211 984.433	0.359	212 021.551	− 0.643
11	6	5		10	6	4	211 984.433	0.359	211 992.300	− 0.487
10	3	8		11	2	9	14 691.111	0.196	12 492.973	− 0.142
10	3	7		11	2	10	27 173.880	0.127	26 823.146	− 0.229
11	2	9		11	2	10	12 158.059	− 0.067	12 366.328	0.100
12	0	12		11	1	11	205 084.712	− 0.274	205 348.155	0.193
12	1	12		11	2	9	33 824.155	0.007	34 878.776	0.011
12	2	11		11	1	10	338 299.524	0.038	337 241.713	− 0.247
12	2	10		11	3	9	7 877.613	− 0.281	9 917.636	0.611
11	3	8		12	2	11	9 370.618	0.208	8 908.261	0.064
12	2	11		12	1	12	184 319.682	− 0.067	183 070.738	− 0.063
12	2	10		12	2	11	16 682.008	− 0.066	16 846.003	0.079
13	2	11		12	3	10	31 132.798	− 0.323	32 996.136	0.844
13	2	12		12	3	9	7 984.916	− 0.285	8 570.750	0.005
13	2	12		13	1	13	191 525.449	− 0.007	190 291.295	− 0.009
13	2	11		13	2	12	22 208.557	− 0.045	22 346.502	0.054
14	0	14		13	0	13	263 004.007	− 0.170	262 960.148	0.070
14	2	13		13	2	12	268 306.534	− 0.092	268 301.429	0.150
14	3	11		13	3	10	271 069.506	− 0.054	270 963.304	0.022
14	4	11		13	4	10	270 145.429	0.099	270 212.803	− 0.409
14	4	10		13	4	9	270 177.731	0.107	270 187.743	0.228
14	2	13		14	1	14	199 287.989	0.047	198 062.333	− 0.018
14	2	12		14	2	13	28 797.955	0.022	28 920.466	− 0.028
14	3	11		14	2	12	217 469.324	0.310	216 534.330	0.119
15	0	15		14	0	14	281 126.966	− 0.153	281082.966	0.109
15	1	15		14	0	14	292 341.387	− 0.178	292 113.552	0.028
15	1	15		14	1	14	278 939.459	− 0.182	278 924.469	0.130
15	2	14		14	2	13	287 247.671	− 0.188	287 236.581	0.137
15	3	13		14	3	12	289 602.934	− 0.053	289 716.284	0.124
15	4	12		14	4	11	289 506.150	0.086	289 585.353	− 0.359
15	2	14		15	1	15	207 596.136	0.107	206 374.431	0.003
15	2	13		15	2	14	36 489.366	0.083	36 602.044	− 0.111
16	2	15		16	1	16	216 435.194	0.171	215 213.998	− 0.009
17	1	17		16	0	16	324 947.593	− 0.208	324 773.489	0.127
17	2	15		16	2	14	334 931.437	0.049	334 904.630	− 0.000
17	2	16		16	2	15	324 997.210	− 0.119	324 977.414	0.154
17	3	14		16	3	13	330 244.177	− 0.040	330 228.150	− 0.057
17	5	12		16	5	11	327 944.827	0.339	327 993.391	− 0.440
17	5	13		16	5	12	327 940.906	0.339	327 997.903	0.155
17	3	14		17	2	15	204 042.958	0.152	203 048.917	− 0.087
18	0	18		17	0	17	335 358.757	− 0.113	335 318.173	0.146
18	2	17		17	2	16	343 802.793	− 0.111	343 779.464	0.144
18	2	16		17	2	15	354 844.436	0.088	354 813.037	− 0.079
18	3	16		17	3	15	347 519.274	− 0.083	347 563.399	0.197
18	5	14		17	5	13	347 288.395	0.326	347 349.381	0.216
18	5	13		17	5	12	347 295.000	0.331	347 345.829	− 0.393
18	3	15		18	2	16	199 331.987	0.104	198 370.341	− 0.034
18	3	15		18	3	16	9 549.303	0.084	9 722.492	0.239

Table 1. (Continued).

J	K_-	K_+	← J	K_-	K_+	freq (A)	cal − obs	freq (E)	cal − obs
19	0	19	18	0	18	353 426.301	− 0.148	353 387.522	0.155
19	1	19	18	1	18	352 251.248	− 0.146	352 232.029	0.180
19	1	18	18	1	17	369 076.622	0.072	368 989.479	− 0.015
19	2	18	18	2	17	362 560.899	− 0.117	362 534.351	0.136
19	2	17	18	3	16	184 899.594	0.114	185 997.854	0.129
19	3	17	18	3	16	366 784.054	− 0.090	366 817.358	0.184
19	5	15	18	5	14	366 645.346	0.276	366 710.791	0.315
19	5	14	18	5	13	366 656.146	0.290	366 708.555	− 0.334
19	3	16	19	3	17	12 873.798	0.168	13 025.707	0.027
20	1	19	19	1	18	387 573.631	0.078	387 483.014	− 0.053
20	2	18	19	2	17	394 433.075	0.183	394 391.024	− 0.202
20	3	17	19	3	16	390 165.306	− 0.009	390 184.181	− 0.073
20	3	17	20	3	18	17 018.103	0.265	17 163.112	− 0.201
21	0	21	20	0	20	389 579.335	− 0.155	389 544.468	0.166
21	1	21	20	1	20	388 773.827	− 0.153	388 753.336	0.207
21	2	20	20	2	19	399 933.104	− 0.101	399 900.871	0.131
21	3	18	21	2	19	186 698.797	− 0.377	185 916.852	0.333
21	3	18	21	3	19	22 087.125	0.375	22 234.413	0.455
22	3	19	22	2	10	183 548.680	− 0.601	182 843.368	0.527
22	3	19	22	3	20	28 175.655	0.583	28 330.732	− 0.737
23	2	22	22	2	21	437 115.382	− 0.172	437 078.311	0.061
23	3	21	22	3	20	443 522.748	− 0.159	443 535.098	− 0.010
23	3	20	23	3	21	35 363.704	0.814	35 529.199	− 1.070
24	1	24	23	1	23	443 436.254	− 0.141	443 414.944	0.213
25	1	25	24	1	24	461 631.470	− 0.124	461 610.131	0.219
27	0	27	26	0	26	498 213.807	− 0.158	498 188.428	0.178
28	1	27	27	1	26	532 210.729	− 0.306	532 130.367	− 0.366
29	0	29	28	0	28	534 457.663	− 0.169	534 434.359	0.230
29	1	29	28	0	28	534 963.911	− 0.301	534 934.267	0.331
29	0	29	28	1	28	533 811.826	− 0.206	533 796.704	0.695
29	1	29	28	1	28	534 317.898	− 0.162	534 297.131	0.277
31	1	31	30	1	30	570 616.043	− 0.246	570 595.978	0.155
32	0	32	31	0	31	588 824.009	− 0.289	588 803.263	0.062

Table 2. Additional measured transitions frequencies (MHz).

J	K_-	K_+	← J	K_-	K_+	S	Frequency	cal − obs
3	2	2	2	1	1	A	197 908.411	− 0.300
10	1	9	9	1	8	A	197 138.479	− 0.197
13	3	10	13	2	11	A	221 295.808	0.281
13	3	10	13	2	11	E	220 446.445	0.138
15	0	15	14	1	14	A	267 725.025	− 0.144
15	0	15	14	1	14	E	267 893.927	0.168
15	1	14	14	2	13	A	203 892.784	− 0.187
15	4	11	14	4	10	E	289 562.343	0.213
16	0	16	15	1	15	A	288 003.796	− 0.132
16	0	16	15	1	15	E	288 144.245	0.187
18	5	13	17	5	12	A	347 295.000	0.331
18	5	13	17	5	12	E	347 345.829	− 0.392
20	3	18	20	2	19	A	265 033.459	0.570
21	3	19	21	2	20	A	270 326.178	0.548
22	3	20	22	2	21	A	276 172.917	0.524
23	5	19	22	5	18	A	444 172.464	0.130
23	5	19	22	5	18	E	444 264.491	0.429
23	2	22	23	1	23	A	291 272.639	0.509
23	3	21	23	2	22	A	282 580.320	0.500
24	3	22	24	2	23	A	289 550.200	0.521
25	4	21	25	3	22	A	288 395.493	− 0.435
28	4	25	27	4	24	A	541 592.794	− 0.525
28	4	25	27	4	24	E	541 648.064	− 0.573
28	5	24	27	5	23	A	541 295.110	− 0.318
28	5	24	27	5	23	E	541 399.228	0.046
30	3	27	29	3	26	A	591 516.380	− 0.094
30	5	25	29	5	24	A	580 812.142	− 0.881
30	5	25	29	5	24	E	580 879.393	0.697
30	5	26	29	5	25	A	580 190.068	− 0.616

quencies after digital filtering (line smoothing, baseline subtraction). Details of this instrument which uses Schottky diodes as well as for the harmonic generation as for the detection have been reported elsewhere [18]. Above 300 GHz the lines were measured with a somewhat different source-modulated spectrometer. The harmonic generation scheme is the same as for the superheterodyne spectrometer: phase-stabilized klystrons (OKI or Varian 50–80 GHz) supply a harmonic generator (Custom Microwave) with fundamental power. The submillimeter power is optically focused through a free-space absorption cell (1 m length) and detected by a Helium-cooled InSb bolometer. After phase-sensitive detection the signal is digitally averaged and processed by a microcomputer in the usual way.

All spectra were measured at room temperature and at pressures below 10 mTorr. The accuracy of the measurements is between 30 kHz and 100 kHz. The measured internal rotation doublets are given in Table 1. The frequencies under 120 GHz were taken from Bauder and coll. [13]. Two more recent low frequency measurements were found in Schrepp and Dreizler [19]. Table 2 lists additional experimental frequencies which were not included into the fit because only one component of the doublet could be measured.

Analysis

The identification was quite straightforward, earlier work provided predictions about approximate frequencies, K doublings and A-E splittings. A least-squares program based on the Internal Axis Method (IAM) was used to calculate the molecular parameters from the observed doublets of Table 1. The basic theory of the IAM for one top molecules is well known [20, 21]. The torsional Hamiltonian H_{ir} is first set up in its own internal axes system (rho representation) and diagonalized numerically for each K value and the eigenvectors are stored to calculate the torsional integrals. The rotational Hamiltonian H_{rr} is set up in the rho representation (using the exact torsional integrals) and added to the diagonal matrix of H_{ir}. The quartic and sextic centrifugal distortion terms are defined in the principal axis system (representation I^r), transformed to the internal axis system and added to the Hamiltonian. The matrix elements of H_{rr} off-diagonal in v are removed by a Van Vleck transformation. And finally the $2J+1$ by $2J+1$ Hamiltonian matrix is diagonalized numerically. Basis function $\exp i\,\alpha(3k+\sigma)$ with k ranging from -10 to $+10$ and a Van Vleck transformation up to $v=4$ were sufficient to obtain stable results within a few kHz. Equal weights were given to the A-type and E-type lines. The resulting parameters are given in Table 3, together with their standard deviations and their correlation coefficients. The differences between observed and calculated frequencies are listed in Table 1. All the parameters are well determined, including I_α which is of the right order of magnitude [22], although the correlation between V_3, and I_α is great, as usual. On the other hand, the correlations between the three internal rotation parameters and

Table 3. Molecular parameters and correlation coefficients for acetaldehyde. $\measuredangle\,(i, a)$: Angle between the inertia axis a and the internal rotation axis i. I_α: Moment of inertia of the methyl group. Standard errors in units of the last digit in brackets.

A	[MHz]	56 611.2742(300)											
B	[MHz]	10 169.04641(207)	.103										
C	[MHz]	9 092.53181(161)	.323	.685									
V_3	[cal/mole]	1 154.687(59)	.094	.140	.244								
I_α	[u.Å^2]	3.20027(15)	−.186	−.015	−.067	−.717							
$\measuredangle\,(i, a)$	[°]	23.844749(63)	.023	−.159	−.304	−.833	.265						
Δ_J	[kHz]	7.54832(154)	.132	.907	.625	.067	.006	−.076					
Δ_{JK}	[kHz]	− 36.330(114)	.357	.400	.330	.145	−.121	−.114	.323				
Δ_K	[kHz]	696.76(269)	.807	−.260	.010	.036	−.122	.037	−.141	−.104			
δ_J	[kHz]	1.24799(97)	.079	.741	.341	.069	−.029	−.088	.827	.281	−.097		
δ_K	[kHz]	9.626(123)	−.216	.010	−.355	.205	−.147	−.188	−.059	.112	−.246	−.222	
Φ_{KJ}	[Hz]	− 31.94(496)	.307	.160	.069	.083	−.085	−.055	.145	.868	.038	.179	.118

the other parameters are very low. This confirms the well known fact that the internal rotation parameters could be determined separately from the splittings without knowing the exact values of the other parameters. The root mean square deviation is 215 kHz for the A-type lines and 294 kHz for the E-type lines, which is definitely greater than the experimental accuracy. A direct determination of the internal rotation parameters V_3, I_α and $\sphericalangle (i, a)$ from the splittings (instead of the frequencies) gives compatible values for these parameters:

$$V_3 = 1154.764(74) \text{ cal/mol},$$
$$I_\alpha = 3.20018(21) \text{ u.Å}^2 \quad \text{and}$$
$$\sphericalangle (i, a) = 23.840819(81)°,$$

the root mean sqaure deviation being 432 kHz for the splittings. This higher rms deviation is not very surprising because we fit only two times less experimental data to four times less parameters (three instead of twelve).

Bauder [23] and de Lucia and coll. [24] have shown that much smaller residual deviations may be obtained if the A- and E-type lines are fitted independently. The differences between the derived parameters of the two symmetry species are due to the effects of the centrifugal distortion on the internal rotation which are completely neglected in the semi-rigid model employed. This procedure should provide more accurate predictions of frequencies. We have tried this method, the internal rotation parameters being kept fixed at the values derived from the fit of the splittings. The results are given in Table 4 together with a conventional centrifugal distortion analysis of the A-lines. To derive the effective parameters the Hamiltonian of Watson (Eq. (68) of [25]) was used. The results are given for the representation I^r in the A reduction. It is obvious that the fit of the A-lines to the centrifugal distortion Hamiltonian of Watson is the worst one because many more parameters are needed and however the rms deviation remains very high: 1583 kHz. On the other hand, the separate fits of the two symmetry states to the internal rotation Hamiltonian give nice results: $\sigma_A = 130$ kHz and $\sigma_E = 245$ kHz and, as expected, the derived constants are significantly different for each symmetry species. This method seems indeed to be best one to accurately predict a spectrum, although in the present case the improvement is not very important.

Finally it may be noted that our value for the barrier to internal rotation is in reasonable agree-

Table 4. Effective molecular parameters for acetaldehyde.

		Fit of the A lines	Fit of the E lines	Fit of the A lines (Watson's Hamiltonian)
A	[MHz]	56 611.2639(214)	56 611.2999(385)	56 932.372(292)
B	[MHz]	10 169.05393(148)	10 169.04011(276)	10 165.1543(154)
C	[MHz]	9 092.53461(112)	9 092.53041(210)	9 099.9607(180)
Δ_J	[kHz]	7.55594(140)	7.54165(262)	7.8152(170)
Δ_{JK}	[kHz]	− 36.621(82)	− 35.870(77)	202.92(177)
Δ_K	[kHz]	696.39(194)	697.13(366)	12 782.5(458)
δ_J	[kHz]	1.25300(70)	1.24357(130)	1.4058(163)
δ_K	[kHz]	9.784(88)	9.483(164)	37.93(368)
Φ_{JK}	[Hz]	0. [a]	0. [a]	77.21(561)
Φ_{KJ}	[Hz]	− 58.07(361)	0. [a]	5 338. (158)
Φ_K	[Hz]	0. [a]	0. [a]	159 907. (1940)
φ_J	[Hz]	0. [a]	0. [a]	0.0363(114)
φ_{JK}	[Hz]	0. [a]	0. [a]	22.02(299)
φ_K	[Hz]	0. [a]	0. [a]	5 854(334)
L_{JKKK}	[Hz]	0. [a]	0. [a]	− 29.80(358)
σ	[MHz]	0.130	0.245	1.583

[a] Fixed value.

ment with the previous experimental determinations and ab initio predictions [26]. Moreover the relatively simple semi-rigid model was sufficient to analyze the spectrum of acetaldehyd which is a low barrier molecule.

Acknowledgements

This investigation has been supported in part by the Centre National de la Recherche Scientifique (ATP PCMI) and by the EPR nord/Pas-de-Calais.

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