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Appendix

Let χ be some measurable quantity which is a function of m_o, V_b, and x_o. V_b and x_o will be held constant. Then let

$$\partial\chi/\partial m_o = f(m_o, V_b, \chi_o)$$

If l_i is the path length over which atom i moves during the tunneling displacement l_H of hydrogen H_6, then the effective mass is

$$m_o = \sum_i m_i(l_i/l_H)^2 = \sum_i m_i\kappa_i \qquad (\kappa_6 = 1)$$

where $\kappa_i = (l_i/l_H)^2$. It will be assumed that κ_i is a constant for each atomic position so that

$$\partial m_o/\partial m_i = \kappa_i$$

and

$$\delta\chi = f\delta m_o = f\kappa_i\delta m_i$$

for small δm_i so

$$\kappa_i = \frac{\delta\chi}{\delta m_i}\frac{1}{f} \text{ and } m_6 = m_o + \frac{1}{f}\sum_{i\neq 6}{}' m_i\frac{\delta\chi}{\delta m_i}$$

where $\delta\chi$ is the change in χ on changing the mass at position i from m_i to $m_i + \delta m_i$. If $\delta\chi$ is the change in the tunneling splitting on isotopic substitution, the equation above for m_o can serve as a tool for finding the value of m_o which yields self consistency.

For example, if $\chi = \Delta E_{01}$ where $\Delta E_{01} = K\Delta\lambda_{01}$ then

$$\begin{aligned} f_1 = \frac{\partial\Delta E_{01}}{\partial m_o} &= \Delta\lambda_{01}\frac{\partial K}{\partial m_0} + K\frac{\partial\Delta\lambda_{01}}{\partial m_o} \\ &= \frac{-2K}{3m_o}\Delta\lambda_{01} + \frac{K\eta}{3m_o}\frac{d\Delta\lambda_{01}}{d\eta} \\ &= \frac{K}{3m_o}\left(\eta\frac{d\Delta\lambda_{01}}{d\eta} - 2\Delta\lambda_{01}\right) = f_1 \text{ (negative)} \end{aligned}$$

Registry No. A, 64516-42-3; A-(D_6), 89066-01-3; A-(D_6D_8), 89066-02-4; A-($D_6D_8{}^{18}O_1{}^{18}O_5$), 89066-03-5; A-($D_6D_7D_9$), 89066-04-6; A-($D_6D_7D_8D_9$), 89066-05-7; A-($D_6D_8{}^{13}C_{2-4}$), 89066-06-8; A-($D_6D_8{}^{13}C_{2-4}{}^{13}C_3$), 89066-07-9; A-($D_6D_8{}^{13}C_2{}^{13}C_4$), 89066-08-0; A-($D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4$), 89066-09-1.

Microwave Spectroscopic Study of Malonaldehyde. 4. Vibration–Rotation Interaction in Parent Species

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Abstract: The microwave spectrum of the parent species of malonaldehyde, which shows Coriolis perturbations only at high J values, has been analyzed with a Hamiltonian which includes both centrifugal distortion and Coriolis terms. The Nielson/Halonen computer program, which treats the Coriolis interaction by introducing a cross term in the inverse inertial tensor, fitted 183 transitions with 20 parameters with excellent accuracy. The fit appears to be unique. Transitions up to $J = 38$ were predicted in the hitherto unexplored 74–85-GHz region. A Stark spectrometer capable of covering this region was devised, using a Raytheon QKK-866 klystron source which could be either swept or phase locked to a harmonic from the R band output of an HP 8460A microwave spectrometer. The same locking arrangement provided accurate frequency measurement. All the transitions were found within 2 MHz of predicted values (<0.5 MHz for $J < 34$). The analysis of all the data gave a tunneling splitting, ΔE_{01}, of 21.583 cm^{-1} and an inverse inertial tensor cross-term coefficient, F, of 45.5 MHz.

Paper 3[2] contains an analysis of Coriolis (or inertial cross product) perturbations in the microwave spectra of several isotopic species of gaseous malonaldehyde (3-hydroxy-1-propenal), particularly those species in which the tunneling atom is deuterium. It was pointed out that the species in which the tunneling atom is not D but H present more difficulty. From intensity measurements on the parent malonaldehyde the tunneling splitting, ΔE_{01}, was estimated to be 26 ± 10 cm^{-1},[3] so useful perturbations would only appear at higher rotational energies, which requires that centrifugal distortion terms be included in the Hamiltonian, in addition to rigid rotor and Coriolis (or inertial cross product) terms. The interaction terms are

$$H = (F + F''J)(P_aP_b + P_bP_a)$$

where F'' is quite small.

Fortunately, a program of this form became available.[4] It has the capability of fitting 34 parameters, A, B, C, Δ_J, Δ_{JK}, Δ_K, δ_J, δ_K, and sextic centrifugal distortion constants for $v = 0$ and separately for $v = 1$, plus ΔE_{01}, F, and F''.

Analysis

The Nielson/Halonen program was applied to two deuterated species, namely (D_6D_8) and ($D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4$), leading to tunneling splittings of 2.884 and 2.828 cm^{-1}, respectively, which agree very well with the results of the CORFIT program.[2] This program[6] includes Coriolis terms but no centrifugal distortion which limits

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Table I. Parameters Obtained from Fitting the Observed Transitions for $\nu = 0$ and of (D_6D_8), ($D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4$), and the Parent Malonaldehyde to the Coupled Two-Level Hamiltonian[a]

	(D_6D_8)		($D_6D_8{}^{13}C_2{}^{13}C_3{}^{13}C_4$)		parent	
	$\nu = 0$	$\nu = 1$	$\nu = 0$	$\nu = 1$	$\nu = 0$	$\nu = 1$
A, MHz	8759.059 (3)	8760.504 (3)	8527.801 (4)	8529.240 (4)	9833.840 (7)	9846.062 (7)
B, MHz	5152.837 (3)	5143.347 (3)	5003.021 (5)	4994.127 (6)	5212.520 (5)	5158.733 (5)
C, MHz	3241.953 (3)	3238.484 (3)	3150.976 (4)	3147.730 (4)	3404.390 (5)	3383.235 (5)
Δ_J, kHz	2.06 (7)	2.14 (7)	1.87 (10)	1.89 (9)	2.75 (3)	2.66 (5)
Δ_{JK}, kHz	−1.50 (17)	−1.74 (18)	−1.29 (24)	−1.95 (25)	−2.87 (10)	−3.33 (15)
Δ_K, kHz	5.27 (12)	4.96 (13)	4.69 (17)	4.85 (18)	6.91 (7)	5.80 (11)
δ_J, kHz	−0.64 (2)	−0.69 (2)	−0.61 (3)	−0.67 (3)	−0.83 (1)	−0.92 (2)
δ_{JK}, kHz	0.69 (3)	0.60 (3)	0.56 (5)	0.63 (5)	1.28 (3)	1.13 (4)
ΔE_{01}, GHz	86.4473 (1)		84.7928 (3)		647.049 (12)	
F, MHz	87.795 (1)		80.25 (1)		45.51 (4)	
F'', kHz	0.855 (7)		0.855[b]		0.84 (2)	
σ, kHz	30		28		15	

[a] Uncertainties, in parentheses, are one standard deviation. σ is the standard deviation of the fit. [b] Assumed.

Table II. Reassigned Frequencies of Malonaldehyde

measured	approximate assignment[3]	new assignment
65 207.84	13(4,10)-13(3,11), $\nu = 0$	13(7,6)-13(6,7), $\nu = 1$
70 650.98	17(7,11)-17(6,12), $\nu = 1$	7(7,0)-7(6,1), $\nu = 0$
59 359.65	21(7,14)-21(6,15), $\nu = 1$	7(6,1)-7(5,2), $\nu = 0$
60 366.27	25(9,16)-25(8,17), $\nu = 0$	11(3,9)-11(2,10), $\nu = 1$
59 444.11	25(9,16)-25(8,17), $\nu = 1$	13(6,8)-13(5,9), $\nu = 1$
86 337.09	39(14,25)-39(13,26), $\nu = 1$	not assigned

Table III. Additional Observed Frequencies of Malonaldehyde

transition	frequency, MHz	difference	VR[a] contribution
	$\nu = 0$		
10(2,9)-9(1,8)	78 637.52	0.16	−0.88
11(7,4)-11(8,3)	80 384.93	0.11	−6.86
11(7,5)-11(8,4)	80 415.53	0.13	6.88
12(4,8)-11(5,7)	84 764.76	0.13	14.25
13(0,13)-13(1,12)	83 492.46	0.22	−2.86
19(4,15)-19(5,14)	83 038.58	0.12	−14.63
19(8,11)-19(9,10)	78 877.22	0.11	−88.14
20(6,15)-20(7,14)	83 555.55	0.03	−44.36
21(5,16)-21(6,15)	83 714.28	0.24	−9.56
23(6,17)-23(7,16)	82 955.63	0.03	3.03
25(7,18)-25(8,17)	80 889.27	0.15	20.78
32(10,22)-32(11,21)	83 184.32	0.41	85.43
35(12,23)-35(13,22)	78 851.96	0.54	−297.45
38(13,25)-38(14,24)	84 327.30	−0.31	−246.97
	$\nu = 1$		
9(3,7)-8(2,6)	84 555.96	0.14	4.82
11(2,10)-10(1,9)	84 768.20	0.01	1.25
12(0,12)-11(1,11)	84 581.67	0.04	0.42
13(8,6)-13(7,7)	79 909.32	0.21	20.43
18(8,10)-18(9,9)	84 546.78	0.21	72.91
21(7,15)-21(8,14)	82 921.38	0.11	66.33
31(11,20)-31(12,19)	79 897.91	−0.10	732.12
32(10,22)-32(11,21)	79 834.56	−0.05	47.66
34(11,23)-34(12,22)	78 560.96	0.14	−159.20
34(12,22)-34(13,21)	84 954.21	0.35	653.50
35(12,23)-35(13,22)	80 672.84	0.33	626.15
36(12,24)-36(13,23)	80 790.45	−0.06	948.76

[a] Vibration-rotation interaction.

its practical application to J values perhaps less than 8. The final parameters of the least-squares refinements are presented in Table I.

One hundred and fifty eight transitions of the parent molecule were previously fairly well fitted with only rigid rotor plus centrifugal distortion (C.D.) terms,[3] but the resulting C.D. constants were quite different for the $v = 0$ and 1 tunneling states. In order to obtain a good fit with the Nielsen/Halonen program, several of the higher J transitions had to be reassigned (see Table II). As a test of the uniqueness of the fit, many different sets of starting parameters were tested, most of which had the same value for the ratio $F^2/\Delta E_{01}$. From the best parameters, transitions of high J were predicted (up to $J = 40$) and several strong transitions were identified which differed from those predicted from the uncoupled refinement of $v = 0$ and 1 states[3] by more than 100 MHz and as much as 2000 MHz. They were mostly in the regions not previously explored for this molecule, 74–85 GHz and 90–99 GHz.

Experimental Section

In order to measure lines in the vicinity of 80 GHz we set up a klystron-based Stark-modulated system which allows both rapid searches over hundreds of MHz with an oscilloscope display including frequency markers and instant transition to phase-locked operation with chart recorder output for line measurement. The rapid searches are provided in a well-known way by an isolated ramp generator synchronized to the horizontal sweep of an oscilloscope and connected to the klystron repeller. Phase-locked operation is accomplished by using the R-band (26.5–40.0 GHz) output of the HP 8460A microwave spectrometer as the local oscillator in the phase-locked loop. Since the ramp generator and the phase-lock synchronizer could be separately disabled, they were placed in series in the following sequence: power supply, ramp generator, synchronizer, klystron repeller with either the ramp or the synchronizer feedback passed to the repeller.

The klystron, a Raytheon QKK-866, covers the range from 78 to 86 GHz. It was connected to an E-H tuner, a 6-dB coupler separating power for the phase-locked loop, an attenuator, a wavemeter, transitions to the X-band Stark cell of the HP 8640A, the Stark cell, transitions to a millimeter waveguide, and a point-contact detector. The sidearm of the coupler was connected to an attenuator and a mixer with mm-wave and R-band inputs whose IF output was connected to the synchronizer. Due to a shortage of components, some mismatches of waveguide size were necessary, requiring the E-H tuner. Most of the mm waveguide was in the 75–110-GHz band, although the klystron output was in the 60–90-GHz band, and some pieces were for 50–75 GHz.

The rapid search mode of operation uses components of the phase-locked system to provide frequency markers shown with absorption lines on the oscilloscope display. The synchronizer, a Microwave Systems PLS-57, has a frequency deviation output which is proportional to the deviation of the incoming IF frequency from the internal 57 MHz. This output thus displays a marker when the HP 8460A R-band frequency is properly related to the klystron output. Coarse measurements of frequency are possible when these markers were used alone. In this mode, it was often possible to scan more than 500 MHz by using the klystron mechanical tuning.

The phase-locked mode uses the rapid search mode to optimize conditions prior to phase lock. The synchronizer frequency output is proportional to the IF strength and differs in phase for lock points above and below the R-band harmonic. With use of this display to adjust the amplitude of the two mixed microwave fields, the desired beat can be maximized and other lock points eliminated or minimized. In most cases, lock could be obtained without difficulty and held long enough for careful measurement in spite of the lack of a search oscillator. Many of the high J lines were not fully modulated even though the Stark modulation fields used were up to 4000 V/cm. The frequencies are believed to be accurate to ±0.2 MHz.

Results

The newly measured rotational transitions are listed in Table III. The transitions of $J < 34$ were all found within less than 0.5 MHz and the higher J transitions within 2 MHz of predicted values. On the other hand, the predictions of the model without

Coriolis interaction were off by 25–307 MHz for the measured transitions of $J > 30$. Further least-squares refinement using the Nielson/Halonen program led to the fit which is shown in Table III. The agreement can be improved using sextic C.D. constants. The final rotational constants, quartic C.D. constants, and Coriolis parameters for parent malonaldehyde are included in Table I. Thus this experiment unambiguously shows the two-level coupled Hamiltonian model to be much more accurate than the separate effective Hamiltonian,[3] and the value of 21.583 cm^{-1} for ΔE_{01} from the microwave spectra should be quite reliable. This gives a period τ in which the H atom oscillates between the two wells of 0.8 ps, where $\tau = h/2\Delta E_{01}$. This result was used in paper 3 to help determine the barrier.

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Registry No. Malonaldehyde, 542-78-9.

Molecular Motions in the Solid Phases of *n*-Heneicosane: A ^{2}H NMR Study

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Abstract: The nature and rate of the molecular motions undergone by heneicosane in the orthorhombic (phase I) and rotator (phase II) phases were investigated. Individual samples of heneicosane, specifically deuterated at positions 2, 4, 6, and 11, were studied at various temperatures by ^{2}H NMR. The spectra of phase I indicate that the central portion of the chain is immobile on the ^{2}H NMR time scale (10^5 s^{-1}). At low temperatures this is also the case at the ends of the chains. However, as the temperature approaches that of the transition to phase II ($T_{\mathrm{I}\to\mathrm{II}}$), a torsional motion is introduced near the ends of the chain. In phase II the data provide evidence for the chains undergoing hindered rotation. They also support the existence of a gauche population concentrated near the chain ends.

The long-chain *n*-alkanes, containing an odd number of carbon atoms, are known to undergo a solid–solid phase transition some 2–15 °C prior to melting.[1-3] The low-temperature phase (phase I) has chains which are all-trans and packed parallel to each other in an orthorhombic unit cell. The higher-temperature phase, phase II (also called the rotator or hexagonal phase), is characterized by an expansion of the unit cell dimensions[4] and the onset of hindered rotation about the chain long axis.[5-8] Andrew has suggested that in phase II there is a cooperative molecular motion around the long axis of the chain, much as in the manner of a set of meshed gears.[5] A ^{1}H NMR relaxation study of the C_{19} *n*-alkane in phase II showed that the relaxation of the methylene protons has contributions from two mechanisms.[6] These are proposed to be a fast rotational reorientation of the entire alkane as a rigid rotator and a slow diffusion of the alkane. The fast reorientation has a mean jump time much less than 10^{-9} s. This corresponds to inelastic neutron scattering results which indicate that the alkane chains exist in an all-trans configuration and reorientation has a mean jump time of approximately 3.5×10^{-12} s.[7]

In a recent ^{2}H NMR study[8] of deuterated nonadecanes, phase II was modeled with an acyl chain undergoing fast ($>10^7$ s^{-1}), 82° jumps between equivalent sites. However, the ^{2}H NMR results also indicated that the chains do not reorient as a rigid rotator. Rather, the ends of the chain undergo higher amplitude torsional motions than the center.

Phase II is also characterized by the appearance of gauche rotamers.[2,3,9,10] Infrared studies have shown that populations are greatest at the ends of the chains and that the gauche population increases as the temperature is increased within phase II.[9] In the case of heneicosane (n-$C_{21}H_{44}$) as many as 8% of the chains contain a gauche rotamer at the 2 positions, just prior to the phase II melt.

In this paper we report on a study of the temperature dependence of the ^{2}H NMR spectra of several specifically deuterated heneicosanes. In phase I the data provide evidence for torsional motions near the chain ends at temperatures near that of the transition from phase I to phase II. In phase II there is evidence for hindered rotation and a positional-dependent gauche population.

Experimental Section

The synthesis of the heneicosanes deuterated at positions 2 (C_{21}-*2,2*-d_2), 4 (C_{21}-*4,4*-d_2), 6 (C_{21}-*6,6*-d_2), and 11 (C_{21}-*11,11*-d_2) has been reported elsewhere.[11] Gas chromatography showed the C_{21}-*11,11*-d_2 to be approximately 95% pure, while all other compounds were better than 99% pure. Mass spectroscopy showed that less than 3.5% of the methylenes were CH^{2}H.[11]

The ^{2}H NMR spectra were acquired on a Bruker CXP-300 spectrometer operating at 46.063 MHz. The quadrupole echo technique[12] with full phase cycling of the radio-frequency pulses was used with a pulse spacing of 50 μs between $\pi/2$ pulses of 6 μs. For phase I spectra

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