Far-Infrared Spectrum, ab Initio, and DFT Calculations and Two-Dimensional Torsional Potential Function of Dimethylallene (3-Methyl-1,2-butadiene)

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The far-infrared and infrared spectra of gaseous dimethylallene (3-methyl-1,2-butadiene), $(CH_3)_2CCCH_2$, were measured as well as the Raman spectra of the compound in all three physical phases. The spectra were assigned using infrared band contours, Raman depolarization ratios and ab initio predicted harmonic frequencies and intensities as criteria. The torsional energy level splittings were determined for the ground state and one torsional excited state from previously published microwave spectra by fitting the frequencies to an effective rotational Hamiltonian for molecules with two periodic large-amplitude motions. The splittings and the data from the far-infrared spectrum were used to derive the two-dimensional torsional potential function of dimethylallene. This function with an effective barrier $V_{3\mathrm{eff}} = 726(4)$ cm^{-1} is compared with the results from the microwave analysis and with the potential function calculated by a number of ab initio methods (among them B3LYP/6-31G(d) and MP2/DZ(d)).

Introduction

The complex torsional far-infrared and Raman spectra of molecules with two symmetric internal rotors have been of interest for some time.[1,2] One of the incentives to study these spectra has been the search for an answer to the question of whether top−top interaction terms in the potential energy function of two-rotor molecules are important. Such terms have been determined for some molecules[1,2] by a combination of far-infrared and Raman spectroscopy and a semirigid model Hamiltonian for coupled internal rotors.[3] Some of them were found to be quite small while others had magnitudes up to about 50% of the barrier height. However, the confidence in the values remained somewhat in doubt because sometimes the coefficients exhibited very large isotope effects. The most likely reason for such irregularities is the fact that the overtone and combination levels of the torsional modes are very often in resonance with other vibrational states and that the resonances are isotope dependent. If such resonances are present, meaningful interaction terms cannot be obtained with the two-dimensional model Hamiltonian. Since then, ab initio calculations for various molecules with two methyl rotors have shown that top−top interaction terms in the potential function are indeed sometimes of considerable magnitude.[4−13] This seems to be the case especially when the methyl groups are attached to the same sp^2 hybridized carbon atom as in acetone,[5,6,9] thioacetone,[7,8] and isobutene (2-methylpropene).[8,11] However, these calculations[4−13] have also shown that the values of these interaction terms depend critically on the method of calculation and the size of the basis set.

Among the molecules with geminal methyl groups on an sp^2 C atom, top−top interaction terms have been determined from far-infrared and Raman data for isobutene (2-methylpropene)[14] and acetone.[2] The torsional frequencies of thioacetone measured by laser-induced phosphorescence have been interpreted in terms of the two-dimensional potential function obtained from ab initio calculations.[7] However, no adjustments of the potential function have been made. Dimethylallene (3-methyl-1,2-butadiene) is another molecule with two methyl groups attached to the same sp^2 carbon atom. Its microwave spectrum has been assigned for the ground state[15,16] and a number of low-lying vibrational excited states.[17] The barrier to internal rotation has been determined from the splitting of the rotational transitions in the ground state (708 cm^{-1})[15] and one torsional excited state (727 cm^{-1}).[17] The infrared and Raman spectra of dimethylallene have been measured and assigned.[18] No torsional transitions have been observed in the Raman spectrum of gaseous dimethylallene, and the far-infrared spectrum of the gas has not been measured. Therefore, Harris and Longshore[18] assigned the torsional frequencies on the basis of the infrared and Raman spectra of the solid sample and derived a barrier to internal rotation of 947 cm^{-1}.

We decided to study the far-infrared and the Raman spectra of gaseous dimethylallene in order to determine the two-dimensional torsional potential function and to compare the spectra with those of the related molecules methylallene (1,2-butadiene)[19] and ethylallene (1,2-pentadiene).[20] Because the spectra did not contain sufficient torsional information, a new method was developed that uses the torsional frequencies as well as splitting data from the rotational spectra (obtained with the effective rotational Hamiltonian for two periodic large-amplitude motions[21]). Ab initio calculations were used to predict the potential function and the vibrational frequencies.

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TABLE 1: Ab Initio Energies[a] (E_h) and Energy Differences between Conformers[b] (cm^{-1}) for Dimethylallene (3-Methyl-1,2-butadiene)

	conformer, (τ_1,τ_2)				
	ee, (0°,0°) E	ss, (60°,60°) ΔE	se, (60°,0°) ΔE	C_s, (30°,−30°) ΔE	C_2, (30°,30°) ΔE
HF/6-31G	3.8655281	1517.20	684.07	646.92	667.07
HF/6-31G(d)	3.9376943	1670.63	750.82	702.84	731.91
MP2/6-31G(d)	4.5750459	1453.18	680.18	532.33	651.69
B3LYP/6-31G(d)	5.2942066	1507.73	688.24	629.84	756.05
HF/DZ	3.8823161	1505.06	649.93	656.92	638.46
HF/DZ(d)	3.9610104	1665.71	724.34	707.97	708.10
MP2/DZ(d)	4.5842136	1568.96	673.30	636.22	665.91
MP2/DZ(d,p)	4.6514104	1570.13	676.74	641.84	668.79

[a] Energy of ee conformer given as $-(E + 190)E_h$. MP2 calculations are frozen core. [b] Methyl groups: ee has both methyl groups eclipsed to the allene group; ss has both methyl groups staggered with respect to the allene group; se has one methyl group staggered and one eclipsed; C_s has both methyl groups rotated by 30° but in opposite directions; C_2 has both methyl groups rotated by 30° in the same direction.

Experimental Section

The 3-methyl-1,2-butadiene sample was purchased from Fluka Chemical Co. It was purified on a low-temperature sublimation column. The far-infrared spectrum was recorded using a Nicolet model 200SXV Fourier transform spectrometer equipped with a vacuum bench, a 6.25 μm Mylar beam splitter and a liquid helium cooled Ge bolometer detector. The sample was contained in a 12 cm cell at a pressure of about 250 Torr. Interferograms for both the sample and reference were obtained as averages of 512 scans and transformed by using a boxcar apodization function. The effective resolution was 0.1 cm^{-1}. The mid-infrared spectrum was measured with a resolution of 0.5 cm^{-1} on a model 14C Digilab Fourier transform spectrometer equipped with Ge/KBr beam splitter, a globar light source and a TGS detector. Raman spectra were recorded using a Cary model 82 spectrophotometer equipped with a Spectra Physics 171 argon ion laser tuned to the 514.5 nm line or a spectrometer consisting of a Spex model 1403 0.85 m double spectrometer combined with the Spex model 1442U third monochromator. The Cary instrument was used to measure the spectrum of the gaseous sample (pressure 300 Torr, standard Cary multipass cell, laser power at sample 1.5 W, resolution 2 cm^{-1}) and to measure depolarization ratios for the liquid phase. The Spex instrument was used to record the Raman spectra of liquid and solid samples in capillary tubes (514.5 nm line, 0.5 W laser power at the sample).

The ab initio calculations were made with the program Gaussian 94 [22] at the Hartree−Fock (HF) level and with electron correlation (second- and third-order Møller−Plesset (MP) perturbation theory) using a range of basis sets. Specifically, the Gaussian sets 3-21G, 6-31G, and 6-31G(d) as well as Dunning−Huzinaga's[23] double-ζ sets DZ, DZ(d), and DZ(d,p) were used (called D95, D95(d), and D95(d,p), respectively, in Gaussian 94 [22]). Density functional theory (DFT) calculations, also made with Gaussian 94, were restricted to the hybrid B3LYP method, although other methods were done for comparison. The energies and geometric parameters were obtained by full optimization of the structure at energy minima, saddle points, or at specified torsional angles of the methyl groups. A number of basis sets have been used in order to calculate the effect of basis set size and electron correlation on the potential energy constants for the torsional motions and on the calculated force fields. The Cartesian force constants have been calculated for different basis sets in both the ab initio and B3LYP methods.

Results

Ab Initio Calculations. The results of the ab initio calculations are presented first since they formed the basis for the assignments of the far-infrared, infrared, and Raman spectra. The fully optimized energies for fixed torsional angles τ_1 and τ_2 obtained for a wide range of ab initio and DFT methods and for a sufficient number of conformations of dimethylallene are presented in Table 1. In the stable conformer, labeled ee, both methyl groups are eclipsed relative to the C═C═C group. The conformation with one methyl group rotated by 60° is labeled es. The highest energy form, ss, has both methyl groups staggered with respect to the C═C═C group. To calculate the relevant top−top coupling terms in the torsional potential energy function, the energies of at least two other conformations are required. Those chosen are labeled C_2 (both methyl groups rotated from the eclipsed position by 30° in the same direction) and C_s (both methyl groups rotated by 30° in opposite directions). The average or effective angle of rotation is actually about 29.2° for both the C_2 and C_s conformations. It was obtained as the average of the dihedral angles of all H atoms in a methyl group. Results for other calculated conformations are not shown.

The full optimization of the geometry with respect to all parameters except the dihedral angles of one H atom in each methyl group resulted in structures of the $C_2C{=}C{=}CH_2$ framework that were slightly distorted from the symmetric structure of the equilibrium conformation. The C═C═C linkage was exactly linear only for the ss, ee, and the C_2 conformations. The C═CH$_2$ group was nonplanar for the es conformation and the C═CC$_2$ part was nonplanar for the C_s conformation. In the C_2 conformation, the dihedral angle of the C═CH$_2$ group with respect to the C═CC$_2$ group was 88.5°.

The coefficients of the two-dimensional torsional potential function

$$\begin{aligned}V(\tau_1,\tau_2) &= (1/2)[V_3(1 - \cos 3\tau_1 + 1 - \cos 3\tau_2) + \\ &\qquad V_6(1 - \cos 6\tau_1 + 1 - \cos 6\tau_2) + \\ &\qquad V_{33}(\cos 3\tau_1 \cos 3\tau_2 - 1) + V'_{33} \sin 3\tau_1 \sin 3\tau_2] \\ &= (1/2)[V_{3\mathrm{eff}}(1 - \cos 3\tau_1 + 1 - \cos 3\tau_2) + \\ &\qquad V_6(1 - \cos 6\tau_1 + 1 - \cos 6\tau_2) + \\ &\qquad V_{33}(1 - \cos 3\tau_1)(1 - \cos 3\tau_2) + \\ &\qquad V'_{33} \sin 3\tau_1 \sin 3\tau_2] \quad (1)\end{aligned}$$

derived from the general form[3] with

$$V_{3\mathrm{eff}} = V_3 - V_{33} \quad (2)$$

were determined by a least-squares fit to the energies in Table 1. They are listed in Table 2.

TABLE 2: Experimental and Theoretical Kinetic and Potential Coefficients of Dimethylallene (cm^{-1})

	V_3	V_{33}	V'_{33}	V_6	V_{3eff}	F	F'
HF/6-31G	758.60	74.53	23.62	−18.18	684.07		
HF/6-31G(d)	835.32	84.49	33.78	−20.54	750.82		
MP2/6-31G(d)	726.73	46.55	124.95	−40.77	680.18	5.4860	−0.0180
B3LYP/6-31G(d)	753.86	65.62	132.04	0.86	688.24	5.4860	−0.0199
HF/DZ	752.53	102.60	−15.02	−13.35	649.93		
HF/DZ(d)	832.85	108.52	6.30	−18.86	724.34		
MP2/DZ(d)	784.48	111.18	35.56	−23.46	673.30	5.4328	−0.0188
MP2/DZ(d,p)	785.07	108.33	32.28	−21.47	676.74		
expt MW[a]					708(11)	5.5556	
expt[b]	766.5(53)	40.3(63)	−9.1(25)	−12.7(20)	726.1(39)	5.512(19)	−0.018[c]

[a] Reference 15; only one parameter varied. [b] This work; standard error in parentheses. [c] Constant during least-squares fit.

TABLE 3: Equilibrium Structure and Rotational Constants[a] of the ee Conformer of Dimethylallene from ab Initio MP2 Calculations and Microwave Spectroscopy

parameter[b]	IC[c]	MP2/ DZ(d)	MP2/6-31G(d)	B3LYP/6-31G(d)	expt MW[d]
C_1C_2	S	1.3265	1.3143	1.3082	1.308
C_2C_3	T	1.3249	1.3164	1.3117	1.308
$C_3C_{4,5}$	U	1.5152	1.5089	1.5149	1.514(1)*
$C_2C_3C_{4,5}$	θ	121.51	121.66	121.69	121.8(1)*
$C_1H_{7,8}$	ν	1.0907	1.0872	1.0894	1.067
$C_2C_1H_{7,8}$	δ	121.13	121.65	121.82	120.9
C_4H_1	r_1	1.0960	1.0921	1.0930	1.091
$C_4H_{2,3}$	r_2	1.1002	1.0961	1.0986	1.088
$C_3C_4H_1$	β_1	111.37	111.38	111.74	110.8
$C_3C_4H_{2,3}$	β_2	110.16	110.41	110.64	111.1
$C_2C_3C_4H_2$[e]	ϕ_2	120.76	120.76	120.86	120.
A		8195.38	8283.56	8222.44	8264.08(25)
B		3554.49	3592.18	3602.27	3614.154(5)
C		2605.28	2632.69	2631.85	2639.494(5)
I_τ[f]		3.2001	3.1693	3.1690	3.13

[a] Bond lengths in ångstroms, angles in degrees, rotational constants *A*, *B*, *C* in MHz. [b] Structural parameters for one methyl group given; the other is equivalent in C_{2v} symmetry. The CH_2 group is perpendicular to the plane containing the carbon atoms. [c] Internal coordinate. [d] Reference 15. All parameters except *U* and θ (with asterisks) were transferred from other molecules. Standard errors in parentheses. [e] $C_2C_3C_4H_3$ is the negative of this. [f] Moment of inertia of one internal rotor (in u·Å^2).

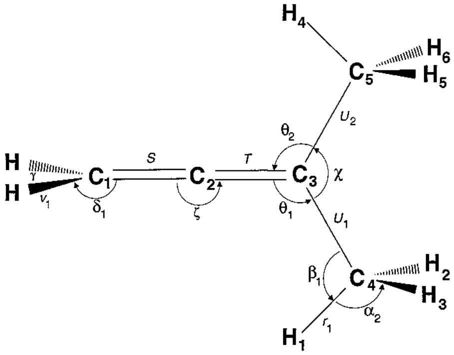

Figure 1. Approximate structure, identification of atoms, and internal coordinate definition for dimethylallene.

The equilibrium structures of dimethylallene (ee conformer) obtained by the various quantum mechanical methods are compared with the reported experimental structure in Table 3. The internal coordinate symbols are defined in terms of the atoms involved; they are illustrated in Figure 1. Bond lengths from RHF calculations, particularly for C═C double bonds with polarization functions included, are usually too short in comparison with experimental bond lengths and are hence not included. Also included in Table 3 are the rotational constants *A*, *B*, *C*, the moment of inertia of the methyl group internal rotor, I_τ. The internal rotation constants *F* and *F*′ calculated from these structures are listed in Table 2.

The vibrational frequencies calculated from unscaled Cartesian harmonic force fields obtained by the RHF, MP2, and B3LYP methods are listed in Table 4. Also included in the table are the frequencies obtained from a scaled MP2/6-31G(d) force field, IR intensities, and Raman activities from unscaled MP2/6-31G(d) and HF/6-31G force fields, respectively, and the potential energy distribution (PED) based on the unscaled MP2/6-31G(d) force field. The symmetry coordinates (C_{2v} point group) used to describe the normal coordinates are defined in Table 5, whereas the internal coordinates used in those definitions are identified in Figure 1.

Spectra and Vibrational Assignments. The far-infrared spectrum (350−130 cm^{-1}) of gaseous dimethylallene is shown in Figure 2. The region between 195 and 140 cm^{-1} is shown in an expanded scale in Figure 3. The Raman spectrum of liquid dimethylallene is shown in Figure 4. The Raman spectra of gaseous and solid dimethylallene and the infrared spectrum of the vapor were essentially identical to the spectra published by Harris and Longshore.[18]

The fundamental frequencies were assigned as shown in Table 4. As a result of the new experimental data (FIR spectrum, depolarization ratios) and the theoretical predictions of the vibrational frequencies, some of the earlier assignments[18] had to be revised. The following evidence supports the current assignment. The *c*-type character of the bands at 439, 247.5, and 174.2 cm^{-1} (ν_{31}, ν_{32}, ν_{33}) is proof that these bands are b_2 vibrations. The microwave investigation of the vibrational excited states[17] showed convincingly that the lowest b_2 vibration (ν_{33}, the infrared active torsional mode) is in Coriolis resonance with the lowest b_1 vibration. Therefore, ν_{25} has to be near 174.2 cm^{-1}. Moreover, the fairly strong depolarized Raman band in this region of the spectrum of the gas has a band contour with a typical gap at 176 cm^{-1} reminiscent of a b-type envelope in an IR spectrum. A similar Raman contour was observed for the much weaker band at 851 cm^{-1} that has an unambiguous

TABLE 4: Vibrational Wavenumbers (cm^{-1}) for Dimethylallene

		HF/6-31G	MP2/6-31G(d)	B3LYP/6-31G(d)	MP2/6-31Gd scaled[a]	H&L[b]	obs gas[c]	obs liquid Raman	obs solid Raman	IR int.[d]	Raman act.[d]	PED
a_1	ν_1	3285	3207	3140	3009	3040	2993		2976	17.3	93.6	97 S_1
	ν_2	3308	3193	3131	2997	2970	3001 R	2989	2985	5.0	224.1	99 S_2
	ν_3	3180	3091	3032	2900	2910	2927	2919	2909	39.3	332.0	97 S_3
	ν_4	2240	2077	2077	2075	1973	1971	1968	1966	8.2	0.6	97 S_4
	ν_5	1667	1571	1543	1487	1471s	1475 R	1472	1472	0.08	50.7	76 S_5, 10 S_9
	ν_6	1634	1522	1501	1441	1437s	1439	1442	1438	1.7	1.4	73 S_6, 11 S_8
	ν_7	1586	1469	1441	1380	1368s	1383 R	1380	1378	0.7	6.4	98 S_7
	ν_8	1447	1352	1334	1309	1290	1289	1288	1285	12.1	41.3	33 S_8, 19 S_6, 19 S_9, 11 S_{10}
	ν_9	1132	1054	1038	1009	1000	1005	1004	1002	8.1	29.9	62 S_9, 20 S_8, 13 S_{10}
	ν_{10}	782	753	740	752	740	724 R	729	730	0.01	28.4	69 S_{10}, 28 S_8
	ν_{11}	366	345	340	343	355	342	351	354	0.1	3.6	89 S_{11}
a_2	ν_{12}	3228	3163	3076	2967	2925s				0.0	8.8	100 S_{12}
	ν_{13}	1636	1537	1504	1442	1451s			1452	0.0	37.6	95 S_{13}
	ν_{14}	1123	1036	1016	977	1072s			986	0.0	10.3	89 S_{14}
	ν_{15}	677	633	616	630	872s			617	0.0	7.5	94 S_{15}
	ν_{16}	171	166	169	166	185s	171.6*			0.0	0.2	100 S_{16}
b_1	ν_{17}	3284	3207	3140	3008	2975	2975		2942	12.6	36.5	97 S_{17}
	ν_{18}	3175	3089	3027	2898	2930	2927	2909	2910	15.8	7.9	97 S_{18}
	ν_{19}	1644	1550	1514	1454	1417s	1423		1423	6.2	0.1	95 S_{19}
	ν_{20}	1571	1452	1425	1369	1370	1370	1367	1368	4.6	8.3	96 S_{20}
	ν_{21}	1321	1265	1220	1248	1072s	1197	1194	1195	3.3	4.5	70 S_{21}, 15 S_{22}
	ν_{22}	1075	1002	977	951	850			957	0.5	5.5	76 S_{22}, 20 S_{21}
	ν_{23}	1060	884	871	884	1193	851	850	852	53.0	2.3	100 S_{23}
	ν_{24}	670	604	612	603	587	582	588	596	7.5	3.8	50 S_{24}, 40 S_{25}
	ν_{25}	208	181	187	181	443s	176 R	187	193	0.2	10.4	60 S_{25}, 42 S_{24}
b_2	ν_{26}	3385	3275	3196	3072	3065	3065	3054	3052	4.7	137.5	100 S_{26}
	ν_{27}	3232	3164	3078	2968	2941s	2948	2940	2925	38.3	209.4	100 S_{27}
	ν_{28}	1650	1552	1520	1456	1456s	1460			15.5	0.5	93 S_{28}
	ν_{29}	1240	1134	1112	1070	1000		1070	1072	0.1	0.7	83 S_{29}, 11 S_{31}
	ν_{30}	1165	1052	1041	992	850	1005			0.1	1.2	92 S_{30}
	ν_{31}	529	439	468	437	267s	439	443	444	0.6	7.9	78 S_{31}, 26 S_{32}
	ν_{32}	287	262	270	261	191	247.5			4.5	0.6	66 S_{32}, 18 S_{31}, 11 S_{33}
	ν_{33}	188	168	182	168	236s	174.2			1.1	0.07	100 S_{33}

[a] Scale factors for force constants: 0.88 for C−H stretches and CH_2, CH_3 deformations, otherwise 1.0. [b] Reference 18, s = solid state. [c] Unmarked: IR spectrum. R: Raman spectrum. *: calculated from fit to torsional data. [d] Infrared intensity in km/mol and PED from unscaled MP2 calculation; Raman activity in Å^4/amu from HF/6-31G calculation.

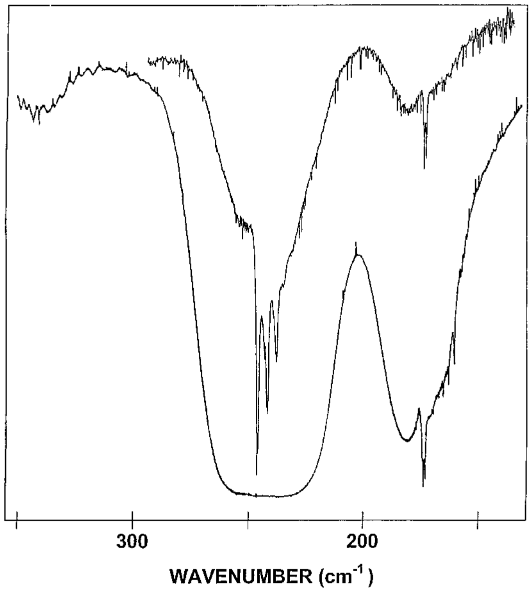

Figure 2. Far-infrared spectrum of gaseous dimethylallene recorded at two different pressures.

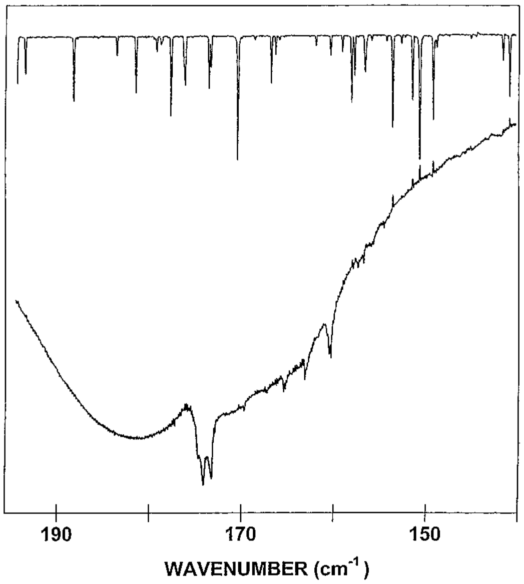

Figure 3. Expanded scale view of the far-infrared spectrum of gaseous dimethylallene. The top trace is the spectrum of water vapor.

b-type counterpart in the IR spectrum. The assignments of these modes (ν_{31}, ν_{32}, ν_{33}, ν_{25}) are confirmed by the fundamental frequencies predicted with the ab initio methods (B3LYP/6-31G(d) and scaled MP2/6-31G(d)). The predicted Raman intensity of ν_{25} is almost 20 times larger than of any other fundamental below 400 cm^{-1} except for the polarized band (ν_{11}) at 342 cm^{-1}. The ab initio force field suggested some reassignments of modes within symmetry species. In the b_1 block, ν_{21} (1197 cm^{-1}) was reassigned as methyl in-plane rock, ν_{22} (957 cm^{-1}, Raman solid) as CH_2 out-of-plane wag, ν_{23} (851 cm^{-1})

TABLE 5: Symmetry Coordinates for Vibrations of Dimethylallene[a]

species	description	coordinate
a_1	CH$_3$ antisymm stretch	$S_1 = 2r_1 - r_2 - r_3 + 2r_4 - r_5 - r_6$
	CH$_2$ symm stretch	$S_2 = v_1 + v_2$
	CH$_3$ symm stretch	$S_3 = r_1 + r_2 + r_3 + r_4 + r_5 + r_6$
	C=C=C antisymm stretch	$S_4 = S - T$
	CH$_2$ scissors	$S_5 = 2\gamma - \delta_1 - \delta_2$
	CH$_3$ antisymm deformation	$S_6 = 2\alpha_1 - \alpha_2 - \alpha_3 + 2\alpha_4 - \alpha_5 - \alpha_6$
	CH$_3$ symm deformation	$S_7 = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3 + \alpha_4 + \alpha_5 + \alpha_6 - \beta_4 - \beta_5 - \beta_6$
	C=C=C symm stretch	$S_8 = S + \mathrm{T}$
	CH$_3$ ip rock	$S_9 = 2\beta_1 - \beta_2 - \beta_3 + 2\beta_4 - \beta_5 - \beta_6$
	C−C−C symm stretch	$S_{10} = U_1 + U_2$
	C−C−C symm bend	$S_{11} = 2\chi - \theta_1 - \theta_2$
	redundancy	$\mathrm{R}_1 = \gamma + \delta_1 + \delta_2$
	redundancy	$\mathrm{R}_2 = \theta_1 + \theta_2 + \chi$
	redundancy	$\mathrm{R}_3 = \alpha_1 + \alpha_2 + \alpha_3 + \beta_1 + \beta_2 + \beta_3 + \alpha_4 + \alpha_5 + \alpha_6 + \beta_4 + \beta_5 + \beta_6$
a_2	CH$_3$ antisymm stretch	$S_{12} = r_2 - r_3 + r_5 - r_6$
	CH$_3$ antisymm deformation	$S_{13} = \alpha_2 - \alpha_3 + \alpha_5 - \alpha_6$
	CH$_3$ op. rock	$S_{14} = \beta_2 - \beta_3 + \beta_5 - \beta_6$
	CH$_2$ twist	$S_{15} = \rho$
	CH$_3$ torsion	$S_{16} = \tau_1 + \tau_2$
b_1	CH$_3$ antisymm stretch	$S_{17} = 2r_1 - r_2 - r_3 - 2r_4 + r_5 + r_6$
	CH$_3$ symm stretch	$S_{18} = r_1 + r_2 + r_3 - r_4 - r_5 - r_6$
	CH$_3$ antisymm deformation	$S_{19} = 2\alpha_1 - \alpha_2 - \alpha_3 - 2\alpha_4 + \alpha_5 + \alpha_6$
	CH$_3$ symm deformation	$S_{20} = \alpha_1 + \alpha_2 + \alpha_3 - \beta_1 - \beta_2 - \beta_3 - \alpha_4 - \alpha_5 - \alpha_6 + \beta_4 + \beta_5 + \beta_6$
	CH$_3$ ip rock	$S_{21} = 2\beta_1 - \beta_2 - \beta_3 - 2\beta_4 + \beta_5 + \beta_6$
	CH$_2$ wag	$S_{22} = \sigma$
	C−C−C antisymm stretch	$S_{23} = U_1 - U_2$
	C=C−C$_2$ ip rock	$S_{24} = \theta_1 - \theta_2$
	C=C=C ip bend	$S_{25} = \zeta$
	redundancy	$\mathrm{R}_4 = \alpha_1 + \alpha_2 + \alpha_3 + \beta_1 + \beta_2 + \beta_3 - \alpha_4 - \alpha_5 - \alpha_6 - \beta_4 - \beta_5 - \beta_6$
b_2	CH$_2$ antisymm stretch	$S_{26} = v_1 - v_2$
	CH$_3$ antisymm stretch	$S_{27} = r_2 - r_3 - r_5 + r_6$
	CH$_3$ antisymm deformation	$S_{28} = \alpha_2 - \alpha_3 - \alpha_5 + \alpha_6$
	CH$_3$ op rock	$S_{29} = \beta_2 - \beta_3 - \beta_5 + \beta_6$
	CH$_2$ rock	$S_{30} = \delta_1 - \delta_2$
	C=C−C$_2$ op wag	$S_{31} = \xi$
	C=C=C op bend	$S_{32} = \zeta'$
	CH$_3$ torsion	$S_{33} = \tau_1 - \tau_2$

[a] Redundancy relations are indicated by R.

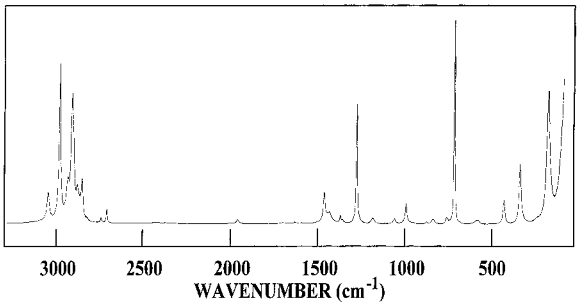

Figure 4. Raman spectrum of liquid dimethylallene.

TABLE 6: Internal Rotation Parameters, Tunneling Energy Coefficients, and Rotational and Centrifugal Distortion Constants for the Vibrational Ground State and the ν_{16} Torsional Excited State of Dimethylallene[a]

parameter	ground state $(v_{16},v_{33}) = (0,0)$	excited state $(v_{16},v_{33}) = (1,0)$
ρ	0.03571(61)	
β/deg.	35.31(14)	
A/MHz	8263.9757(28)	8251.465(63)
B/MHz	3614.1873(13)	3613.8736(21)
C/MHz	2639.48746(96)	2638.3845(19)
Δ_J/kHz	0.4757(82)	
Δ_{JK}/kHz	10.325(72)	10.73(32)
Δ_K/kHz	−1.69(30)	
δ_J/kHz	0.1536(20)	0.1496(70)
δ_K/kHz	6.054(37)	
$\epsilon_{\nu 10}$/MHz	−4.18(13)	86.4(29)
n[b]	113	67
σ/MHz[c]	0.040	

[a] Standard errors in parentheses. Excited-state values not listed are identical to the corresponding ground-state values. [b] Number of frequencies included in the least-squares fit. [c] Standard deviation.

as C—C—C antisymmetric stretch, and ν_{25} (176 cm^{-1}) as C=C=C in-plane deformation. In the b$_2$ block, ν_{29} (1072 cm^{-1}, Raman solid) was assigned as CH$_3$ out-of-plane rock, ν_{30} (1005 cm^{-1}) as CH$_2$ rock, ν_{31} (439 cm^{-1}) as C=CC$_2$ out-of-plane wag, ν_{32} (247.5 cm^{-1}) as C=C=C out-of-plane deformation, and ν_{33} (174.2 cm^{-1}) as CH$_3$ torsion. In the a$_1$ block, the assignments of ν_1 and ν_2 were based on the comparison of predicted and observed Raman intensities. Among the a$_2$ vibrations, only the frequency of ν_{16} (CH$_3$ torsion) is reasonably well established from the torsional analysis (see below). The 986 and 617 cm^{-1} bands (Raman solid) were assigned to ν_{14} and ν_{15}, respectively, on the basis of the predicted frequencies.

Torsional Potential Function. The band near 170 cm^{-1} (Figure 3) shows a number of c-type Q-branches superimposed on the rotational band envelope. They must originate from the infrared active torsional mode and its hot transitions. Since three or four torsional frequencies from the far-infrared spectrum were insufficient to determine a two-dimensional torsional potential function based on experimental data, additional information in the form of energy differences between torsional substates was obtained from the splittings of rotational transitions in the microwave spectrum. For that purpose, the microwave frequencies reported in the literature for the vibrational ground state[15,16] and the first excited state of the a$_2$ torsional mode (ν_{16})[17] were analyzed by the effective rotational Hamiltonian for two periodic large-amplitude motions.[21] The observed frequencies for both states were used simultaneously in a global least-squares fit to determine rotational constants, quartic distortion constants (I^r representation, A reduction[24]), and tunneling energy parameters for each state, as well as the common parameters ρ (internal rotation parameter) and β (angle between the ρ axes and the a principal inertial axis). Because a smaller number of higher J transitions were reported for the excited state, three distortion constants were forced to be identical to the respective ground-state constants. The results of the least-squares fit are shown in Table 6.

The tunneling energy parameters $\epsilon_{\nu 10}$ in that table are coefficients of the Fourier expansion for the internal rotation energy[21]

$$E_{\nu\sigma_1\sigma_2} = \epsilon_{\nu 00} + 2\sum_{q>0}\{C_{qq}\epsilon_{\nu qq} + C_{q-q}\epsilon_{\nu q-q} + \sum_{q'=-q+1}^{q-1}(C_{qq'} + C_{q'q})\epsilon_{\nu qq'}\} \quad (3)$$

where

$$C_{qq'} = \cos(2\pi(q\sigma_1 + q'\sigma_2)/n) \quad (4)$$

Subscript ν stands for a set of vibrational quantum numbers. The symmetry quantum numbers σ_1 and σ_2 may assume the allowed values 0, 1, or 2 because $n = 3$ for methyl groups. The levels with $(\sigma_1,\sigma_2) = (0,0)$ correspond to the nondegenerate AA substates (Γ^{00} in ref 3). The combinations (0,1), (0,2), (1,0),

TABLE 7: Torsional Energy Differences and Transitions, Residuals, and Relative Intensities for Dimethylallene

transition $(v_{16},v_{33})\ \sigma_1\sigma_2 - (v_{16},v_{33})\ \sigma_1\sigma_2$	obs	calc	obs − calc	unc[a]	units	wr[b]	int[c]
(0,0) 01 − (0,0) 00 = $\Delta_{(0,0)01}$	12.534	11.954	0.580	0.38	MHz	1.527	
(0,0) 11 − (0,0) 00 = $\Delta_{(0,0)11}$	25.069	23.908	1.161	1.52	MHz	0.764	
(0,0) 12 − (0,0) 00 = $\Delta_{(0,0)12}$	25.069	23.908	1.161	1.52	MHz	0.764	
(1,0) 01 − (1,0) 00 = $\Delta_{(1,0)01}$	−259.122	−274.257	15.135	8.58	MHz	1.764	
(1,0) 11 − (1,0) 00 = $\Delta_{(1,0)11}$	−518.244	−546.322	28.078	34.32	MHz	0.818	
(1,0) 12 − (1,0) 00 = $\Delta_{(1,0)12}$	−518.244	−546.325	28.081	34.32	MHz	0.818	
(0,1) 00 − (0,0) 00	174.22	174.15	0.074	0.2	cm^{-1}	0.372	51
(0,2) 00 − (0,1) 00	173.41	173.39	0.022	0.2	cm^{-1}	0.109	28
(0,3) 00 − (0,2) 00	163.04	163.08	−0.039	0.2	cm^{-1}	−0.197	16
(1,1) 00 − (1,0) 00	160.38	160.44	−0.062	0.2	cm^{-1}	−0.308	16
(1,0) 00 − (0,0) 00		171.64			cm^{-1}		
(2,0) 00 − (0,1) 00	156.65	158.83			cm^{-1}		10
(3,0) 00 − (1,1) 00		147.35			cm^{-1}		7
(1,2) 00 − (1,1) 00	174.73	174.36			cm^{-1}		5
(2,1) 00 − (2,0) 00		146.29			cm^{-1}		7
(0,3) 00 − (2,0) 00		177.64			cm^{-1}		4

[a] Relative uncertainty or standard error (see text). [b] Weighted residual (dimensionless). [c] Relative intensity (arbitrary units, see text).

and (2,0) make up the 4-fold degenerate EE (Γ^{01}) sublevel whereas the pairs (1,1), (2,2) and (1,2), (2,1) correspond to the doubly degenerate AE (Γ^{11}) and EA (Γ^{12}) levels, respectively. The energy differences between the torsional substates, in the present case given by

$$\begin{aligned}\Delta_{\nu01} &= E_{\nu01} - E_{\nu00} = -3\epsilon_{\nu10}\\ \Delta_{\nu11} &= E_{\nu11} - E_{\nu00} = -6\epsilon_{\nu10}\\ \Delta_{\nu12} &= E_{\nu12} - E_{\nu00} = -6\epsilon_{\nu10}\end{aligned} \tag{5}$$

were included in a weighted least-squares fit with the far-infrared frequencies to determine the two-dimensional potential function. A program similar to the one described earlier[3] was used. The data were weighted by the squared inverses of the estimated uncertainties assumed as follows: 0.2 cm^{-1} for the far-infrared frequencies, standard errors for the differences $\Delta_{\nu01}$, and doubled standard errors for $\Delta_{\nu11}$ and $\Delta_{\nu12}$. The parameters $V_{3\mathrm{eff}}$, V_{33}, V'_{33}, V_6, and F of the Hamiltonian

$$H = (1/2)(p_1Fp_1 + p_2Fp_2 + p_1F'p_2 + p_2F'p_1) + V(\tau_1,\tau_2) \tag{6}$$

where p_1 and p_2 are the angular momenta conjugate to the internal rotation variables, F and F' are the kinetic energy coefficients, and $V(\tau_1,\tau_2)$ is the potential function defined in eq 1, were adjusted in a fit starting with the MP2/DZ(d) potential and kinetic coefficients. The kinetic coupling coefficient F' was not varied. The results are shown in Table 7 (energy differences, frequencies and residuals) and Table 2 (potential and kinetic parameters).

Discussion

According to the ab initio calculations and as in the cases of acetone[5,6,9] and thioacetone,[7] the interaction terms V_{33} and V'_{33} in the two-dimensional potential function for dimethylallene are not negligible as their magnitudes relative to V_3 are considerable. As expected, the values of all potential coefficients depend on the size of the basis set and the level of calculation. However, the coefficients change by less than 4 cm^{-1} between the MP2/DZ(d) and MP2/DZ(d,p) calculations although the energy of the equilibrium conformation differs by 0.067 E_h (almost 15 000 cm^{-1}). Five of eight calculations in Table 2 predict effective barriers between 670 and 690 cm^{-1}. V_{33} varies from 46 to 112 cm^{-1}, whereas the variation in V'_{33} is even larger (−15 to +132 cm^{-1}). Only the B3LYP/6-31G(d) calculation produced a very small V_6 term, the other ones ranging from −13 to −41 cm^{-1}. The reasons for the large variability of the interaction terms V_{33} and V'_{33} among the basis sets and methods are not known. From the limited experience gained during this investigation, it seems that the choice of the method (HF vs MP2) has a large effect on V'_{33}. The basis set size seems to affect both V'_{33} and V_{33}. Unfortunately, there are no reliable experimental determinations of such coefficients in the literature for any molecule.

The structural parameters of dimethylallene for three calculations are compared in Table 3 with the structure proposed in the microwave investigation.[15] Because the rotational constants of only one isotopomer were available in that study, only two parameters had been determined. The remaining parameters had been transferred from cognate molecules. For that reason, a detailed comparison of experimental and theoretical results is not warranted. Bearing in mind the conceptual differences between the ab initio and the observed ground-state rotational constants, the agreement between the MP2/6-31G(d) and B3LYP/6-31G(d) results and the experimental constants is gratifying. In general, the B3LYP/6-31G(d) structures agree better with experimental (r_0 or r_s) structures than MP2/6-31G(d) structures, particularly if the structures contain double or triple bonds.[25]

With the additional data from the far-infrared spectrum and the normal frequencies predicted from the ab initio calculations, an almost complete assignment of the normal modes is now available for all symmetry species except for the a_2 block containing the infrared inactive modes. Whereas the normal-mode frequencies obtained in the HF calculations are always much too high, the MP2 wavenumbers generally are significantly lower. However, the best predictions of normal-mode frequencies at a comparable level were obtained by the DFT hybrid method B3LYP/6-31G(d), in agreement with earlier observations.[26−29] This is also true for the stretching vibrations of multiple bonds, which tend to be low in MP2 calculations because of the notoriously long bond lengths of multiple bonds calculated by this method. In the case of C≡C bonds, the MP2 wavenumbers may be even lower than observed[30] whereas the B3LYP wavenumbers are a little higher than the experimental data as expected because of anharmonicity. The frequencies involving the C═C═C group are also greatly reduced on going from the HF column in Table 4 to the MP2 column, but it appears in this case (or cases involving C═C double bonds) that the MP2 wavenumbers are near to those from B3LYP calculations. The frequencies of the in-plane and out-of-plane C═C═C bending modes are about 26 cm^{-1} lower and 72 cm^{-1}

lower, respectively, than in the spectrum of methylallene.[19] In ethylallene,[20] the in-plane mode of the gauche conformer appears at the same frequency as in dimethylallene whereas the mode of the cis conformer is 25 cm^{-1} lower. The out-of-plane bending vibrations of both conformers could not be assigned with certainty.

The ab initio calculations were valuable during the assignment of the torsional far-infrared bands because they established that the separation between the torsional modes was likely much smaller than was suggested by the previous microwave[17] and far-infrared[18] investigations. Of even greater importance for the determination of the two-dimensional potential function were the differences between the torsional sublevels derived from the microwave frequencies with the effective rotational Hamiltonian for two periodic large-amplitude motions.[21] It also allowed the derivation of a potential function that is compatible with both kinds of experimental data. The fit of sublevel splittings and far-infrared transitions is excellent. The results depend, of course, to some extent on the relative weights of torsional and splitting data. It was very satisfying to notice that the fit converged smoothly and that the final potential coefficients and the internal rotation constant F were comparable to the quantities predicted by the ab initio calculations. The effective barrier height (726.1(39) cm^{-1}) was somewhat higher than the result obtained in the original microwave investigation (708(11) cm^{-1}),[15] which in turn was higher than most of the ab initio predictions (670−690 cm^{-1}, Table 2). The barrier is therefore about the same as in 2-methylpropene (isobutene),[14] only slightly above the propene barrier (694 cm^{-1}),[31] but 170 cm^{-1} higher than in 1,2-butadiene (methylallene).[19]

After the least-squares fit, the complete spectrum was recalculated. Some of the more intense lines are also listed in Table 7 by assignment and frequency. To estimate the relative intensities of the far-infrared transitions, the squares of the matrix elements of the operator

$$\sin 3\tau_1 - \sin 3\tau_2$$

(consisting of the leading terms of the most general form for the c-component of the dipole moment) were multiplied by the appropriate Boltzmann population factors at 298 K. This allowed us to tentatively assign two other weak peaks in the far-infrared spectrum, as listed in Table 7. According to the prediction, the a_2 torsional mode (ν_{16}) is only 2.5 cm^{-1} lower than the infrared active torsional fundamental ν_{33}. In view of the fact that the three lowest fundamentals of dimethylallene occur within less than 5 cm^{-1} (because the b_1 skeletal deformation ν_{25} is only 1.6 cm^{-1} higher or lower than ν_{33} [17]), it is rather surprising that no difficulties were encountered in fitting the hot transitions (0,2) ← (0,1) and (0,3) ← (0,2) whose upper levels have numerous chances of being in Fermi resonance with a large number of energy levels.

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