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Conformational Analysis. 7. 1,2-Difluoroethane. An Electron-Diffraction Investigation of the Molecular Structure, Composition, Trans–Gauche Energy and Entropy Differences, and Potential Hindering Internal Rotation

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Abstract: The molecular structure of 1,2-difluoroethane has been investigated by electron diffraction from the gas at nozzle-tip temperatures of 22, 203, and 420 °C. Two distinct conformers were identified, a lower energy gauche form (observed in earlier diffraction studies) and a higher energy trans form. Analyses of the gauche structure were carried out by a least-squares procedure based on a simultaneous fitting of rotational constants (one isotopic species) and the diffraction data assuming the two conformers to differ only in torsion angle. Three types of models differing in manner of handling the torsional problem were tested. The values of the bond lengths and bond angles obtained from these models were essentially identical. The energy and entropy differences, the rotameric compositions, and the values of certain other temperature-dependent properties as deduced from the three models do not agree quite so well, but are consistent when account is taken of the associated uncertainties. At 22 °C, after corrections for the effects of vibrational averaging, the bond lengths (r_a), bond angles, and root mean square amplitudes of vibration with uncertainties (2σ) from the preferred model were found to be r(C–H) = 1.103 (4) Å, r(C–F) = 1.389 (2) Å, r(C–C) = 1.503 (3) Å, ∠CCF = 110.3 (1)°, ∠CCH = 111.0 (10)°, ∠HCH = 108.5 (16)°, ∠FCCF = 108.7 (17)°, l(C–H) = 0.075 (5) Å, l(C–F) = 0.053 (3) Å, l(C–C) = 0.062 (9) Å, l(C·F) = 0.069 (3) Å, and l(C·H) = 0.106 (10) Å. The torsional potential was represented by the function $2V = \Sigma V_i(1 - \cos i\phi)$, $i = 1, 2, 3$; the averages of the values of the coefficients refined at the three temperatures are $V_1 = 0.67$ (42), $V_2 = -2.53$ (25), and $V_3 = 2.21$ (28), all in kilocalories per mole, from which the rough values 4.52 (72) and 2.36 (58) kcal/mol are calculated respectively for the gauche–gauche and gauche–trans barriers. The rotameric compositions at 22, 203, and 420 °C are calculated to be 4.0 (18), 10.3 (24), and 19.4 (29)% trans from which the energy and entropy differences are found to be $E_t° - E_g° = 1.76$ (51) kcal/mol and $S_t° - S_g° = 0.97$ (96) cal K^{-1} mol^{-1}. Rough values for the torsional frequencies calculated from the potential function are 128 (gauche) and 84 cm^{-1} (trans). The structure is discussed.

Elementary considerations predict that the 1,2-dihaloethanes can exist in two conformations, a trans and a gauche, as illustrated by Figure 1. It is generally agreed that the trans form is the more stable in the chlorine, bromine, and iodine compounds, and electron-diffraction patterns made from the vapors of these substances[1,2] clearly show the presence of both forms in proportions which depend on the sample temperature. In the case of 1,2-difluoroethane, however, the gauche form is the more stable; moreover, it predominates to such extent at room temperature as to make detection of the trans form extremely difficult. Thus, according to an unpublished electron-diffraction investigation[3] room temperature samples of 1,2-difluoroethane are 85–96% gauche molecules, and data from another study[4] by the same method were successfully interpreted in terms of gauche molecules only.

The measurement of conformational equilibria at different temperatures by gas electron diffraction and the deduction of the energy and entropy differences of the species have received considerable attention in this laboratory. The case of 1,2-difluoroethane interested us because there is apparently no experimental value for the entropy difference and because the experimental estimates of the energy difference $E_t° - E_g°$ vary considerably: in kilocalories per mole these are 0.59–1.42[3] and 1.7[4] (lower limit) from the electron-diffraction work, 0.60[5] and 1.98[6] from recent spectroscopic studies, and −1.42[7] and 0.6[8] from NMR studies. It was felt that our technique of measuring the temperature dependence of the rotameric composition (the older diffraction work was done only at room temperature) would yield a value for the entropy difference and remove the uncertainty in the energy difference. We also hoped to settle the matter of some discrepancies between the structural results from the two older diffraction investigations.

When our work had been completed, we learned of the results of a new study of 1,2-difluoroethane from the Oslo laboratory.[9] The energy and entropy differences based on experiments at two temperatures were found to be $E_t° - E_g° = 0.93$ ($\sigma = 0.41$) kcal/mol and $S_t° - S_g° = 1.5$ ($\sigma = 0.8$) cal mol^{-1} K^{-1}.

Experimental Section

1,2-Difluoroethane was prepared from ethylene glycol by the procedure of Edgell and Parts[10] as modified by Butcher et al.[11] The IR spectrum of the product was virtually identical with that reported by Harris et al.[6] and was assumed to have only insignificant amounts of impurities.

About 30 diffraction photographs were made in the Oregon State

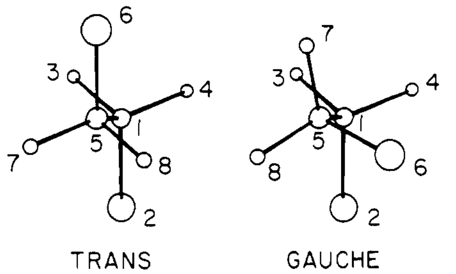


Figure 1. Atom numbering for *trans*- and *gauche*-1,2-difluoroethane.

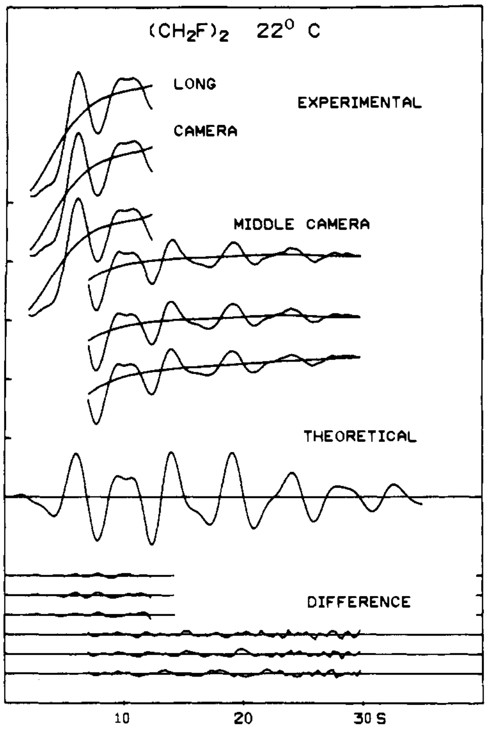


Figure 2. Intensity curves. The experimental curves are s^4I_T shown superimposed on the final backgrounds. The theoretical curve is sI_m for the final CP model. The difference curves are the experimental minus the theoretical.

apparatus at temperatures of 22, 203, and 420 °C. Experimental conditions were as follows: sector shape, r^3; plates, 8 × 10 in. Kodak projector slide medium contrast; development, 10 min in D-19 diluted 1:1; ambient apparatus pressure during exposure, 4.4×10^{-6} to 1.4×10^{-5} Torr; exposure times, 40–200 s; beam currents, 40–49 μA; nozzle-to-plate distances, 75.037–75.131 ("long camera") and 30.117–30.157 cm ("middle camera"); electron wavelengths, 0.058 19–0.058 27 Å; wavelength standard, CO_2 with r_a(C–O) = 1.1646 Å and r_a(O·O) = 2.3244 Å.

Analysis of the structure at each temperature was based on three plates from the long and three from the middle camera distance. The procedures for obtaining the scattered intensity distribution have been described.[12] Calculated[13] backgrounds were subtracted from the intensity data from each plate to provide molecular intensities in the form

$$sI_m = k \sum_{i \neq j} A_iA_jr_{ij}^{-1} \cos|\eta_i - \eta_j| V_{ij} \sin s(r_{ij} - \kappa_{ij}s^2) \quad (1)$$

The ranges of the data were $2.0 < s < 12.25$ Å^{-1} (long distance) and $7.0 < s < 30.0$ Å^{-1} (middle distance) and the data interval was $\Delta s = 0.25$ Å^{-1}. Figure 2 shows curves of the total scattered intensities and the final background for the experiment at 22 °C. The corresponding curves for the other temperatures and all the data are available as supplementary material.

Radial distribution curves were calculated from composites[12] of the molecular intensities according to

$$rD(r) = \frac{2}{\pi}\Delta s \sum_{s=0}^{s_{max}} I'(s) \exp(-Bs^2) \sin rs \quad (2)$$

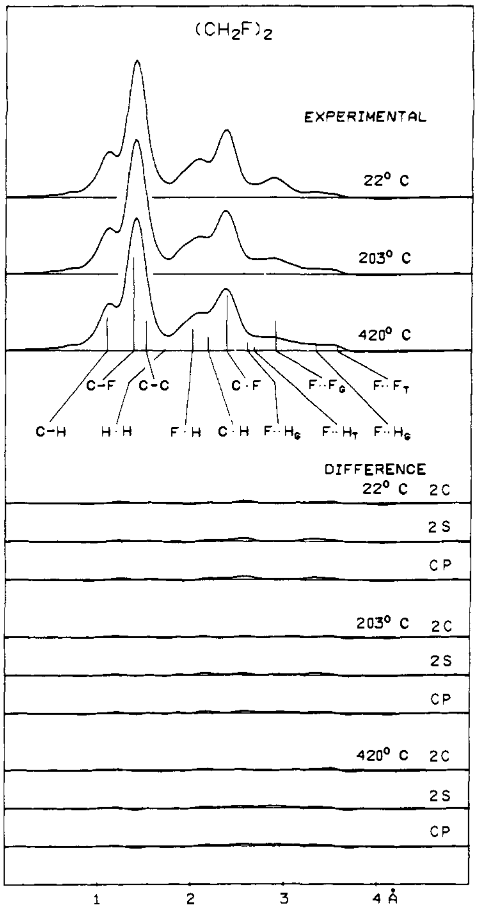


Figure 3. Radial distribution curves. The experimental are calculated from composites of molecular intensities from the two camera distances.

with $I'(s) = sI_mZ_CZ_FA_C^{-1}A_F^{-1}$ and B usually equal to 0.0025 Å^{-1}. The A_i (equal to s^2F_i) used here and in later intensity calculations were obtained[13] from tables[14] of the scattering amplitudes F. For experimental $rD(r)$ curves data in the unobserved or uncertain region $s < 2.00$ Å^{-1} were taken from theoretical curves. The final radial distribution curves are shown in Figure 3.

Structure Analysis

Radial Distribution Curves. The peaks of the radial distribution curves were easily identified as arising from the distances marked by the vertical lines. It is evident from the relative areas of the peaks at about 2.9 and 3.5 Å that the gauche conformer predominates at all temperatures. It is also evident from the changes in these relative areas that the amount of trans conformer is increased substantially by increasing the temperature.

Choice of Models. The modeling of a system of a pair of rotational conformers for analysis of the structures and assessment of the composition may be done at different levels within the classical approximation. Several of these have been used in earlier work from this laboratory, but not in the same investigation. It seemed worthwhile to look into the effect of model type on parameters of interest; accordingly, we selected three for the 1,2-difluoroethane work. The simplest, which might be termed the "two-conformer" model (2C), represents the system as comprising two types of molecules differing essentially only in their torsion angles. The effects of molecular vibration are treated by applying the harmonic vibration approximation $V_{ij} = \exp(-l_{ij}^2s^2/2)$ to all distances including those affected by torsional motion. Clearly, the 2C model would be expected to apply best to molecules having high torsional barriers and narrow potential minima. The "double-σ" model (2S) takes account of large-amplitude torsion for each of the two conformers by a separate treatment of the

Table I. Symmetry Coordinates, Force Constants, and Wavenumbers for *gauche*-1,2-Difluoroethane

		force constants		wavenumbers	
species	symmetry coordinates	i,j	F_{ij}	ω_{obsd}	$\omega_{obsd} - \omega_{calcd}$
A	$S_1 = 1/2\Delta(r_{13} + r_{14} + r_{57} + r_{58})$	1,1	4.906	2997	0
	$S_2 = 1/2\Delta(r_{13} - r_{14} + r_{57} - r_{58})$	2,2	4.754	2959	0
	$S_3 = 1/\sqrt{2}\Delta(r_{12} + r_{56})$	3,3	7.039	1409	−11
	$S_4 = \Delta(r_{15})$	4,4	4.728	1285	9
	$S_5 = 1/2\Delta(\beta_{513} + \beta_{514} + \beta_{157} + \beta_{158})$	5,5	0.437	1119	−2
	$S_6 = 1/2\Delta(\beta_{513} - \beta_{514} + \beta_{157} - \beta_{158})$	6,6	0.577	1067	11
	$S_7 = 1/\sqrt{2}\Delta(\beta_{512} + \beta_{156})$	7,7	1.153	864	−1
	$S_8 = 1/\sqrt{12}\Delta(-\alpha_{213} - \alpha_{214} + 2\alpha_{314} - \alpha_{657} - \alpha_{658} + 2\alpha_{758})$	8,8	0.462	717	−3
	$S_9 = 1/2\Delta(\alpha_{213} - \alpha_{214} + \alpha_{657} - \alpha_{658})$	9,9	0.575	327	0
	$S_{10} = 1/3\Delta(\tau_{2156} + \tau_{3157} + \tau_{4158})$	10,10	0.135	148	0
		3,4	0.79		
B	$S_{11} = 1/2\Delta(r_{13} + r_{14} - r_{57} - r_{58})$	11,11	5.003	3000	0
	$S_{12} = 1/2\Delta(r_{13} - r_{14} - r_{57} + r_{58})$	12,12	4.765	2984	0
	$S_{13} = 1/\sqrt{2}\Delta(r_{12} - r_{56})$	13,13	7.339	1458	0
	$S_{14} = 1/2\Delta(\beta_{513} + \beta_{514} - \beta_{157} - \beta_{158})$	14,14	0.891	1376	−1
	$S_{15} = 1/2\Delta(\beta_{513} - \beta_{514} - \beta_{157} + \beta_{158})$	15,15	0.799	1244	−2
	$S_{16} = 1/\sqrt{2}\Delta(\beta_{512} - \beta_{156})$	16,16	1.129	1045	0
	$S_{17} = 1/\sqrt{12}\Delta(-\alpha_{213} - \alpha_{214} + 2\alpha_{314} + \alpha_{657} + \alpha_{658} - 2\alpha_{758})$	17,17	0.530	896	3
	$S_{18} = 1/2\Delta(\alpha_{213} - \alpha_{214} - \alpha_{657} + \alpha_{658})$	18,18	0.727	499	0
		13,14	−0.139		
		13,17	−0.187		

effects of torsional motion: the distribution of pseudoconformers is assumed to have the form $P(\phi) = Q^{-1}\exp(-\phi^2/2\sigma_\phi^2)$ around the two potential minima $\phi_0(1)$ and $\phi_0(2)$. Each of the pseudoconformers is regarded as rigid in a torsional sense and "frame" amplitudes are assigned to each distance. The number of pseudoconformers necessary to represent the distribution satisfactorily is determined by the amplitude of the motion; we have found that in most cases a spacing of $\frac{1}{2}\sigma_\phi$ over the range $-2\sigma_\phi < \Delta\phi < 2\sigma_\phi$ (nine terms) is adequate, but occasionally more are needed. The quantities $\sigma(1)$ and $\sigma(2)$, the root mean square amplitudes of torsional motion for the two conformers, are ordinarily handled as refinable parameters. Both the 2S and the "single σ" or 1S model (obviously the same approach applied to only one conformer) are substantially better approximations of torsional motions than the 2C model, but the usefulness of the results depends on the adequacy of the harmonic approximation for the torsion. In the "cosine potential" model (CP) the distribution of molecules around the torsional coordinate is taken to be determined by the function

$$P(\phi) = Q^{-1}\exp(-V(\phi)/RT) \tag{3}$$

with

$$V(\phi) = \tfrac{1}{2}\sum_i V_i(1 - \cos i\phi), \quad i = 1, 2, 3, \ldots \tag{4}$$

Pseudoconformers are normally included at 5-10° angle intervals throughout the nonredundant region of the torsional coordinate and each is assigned a set of frame amplitudes. The V_i are in principle refinable parameters. The CP model would seem to be the best for describing the distribution of molecules around the torsional coordinate, but the interpretation of the results in terms of types of molecules, say distinct conformers, even within the classical approximation is not so simple as with the other models.

Structure Refinements. The structures were determined by fitting intensity functions calculated from eq 1 to the observed intensities by least squares[15] and, in the final stages, by this and a simultaneous fitting of the corresponding calculated rotational constants to those observed from microwave spectroscopy.[11] In all the work the conformers (and pseudoconformers) were assumed to have the same structures except for torsion angle and the harmonic approximation ($V_{ij} = \exp(-l_{ij}^2 s^2/2$; $\kappa = 0$) was adapted for frame amplitudes. The intensity data from each plate, weighted equally, were fitted simultaneously, i.e., without first being formed into averages. When the rotational constants were included, they were weighted 100 times as heavily as each diffraction datum: tests showed that over a rather broad range the relative weighting of the two types of data did not have an important effect on the results.

It is well known that the effects of molecular vibration operate to make the set of distances appearing in eq 1 geometrically inconsistent; i.e., ratios of distances calculated from the equilibrium structure do not agree with the corresponding ratios of r_a distances. Moreover, these thermally averaged r_a distances are inappropriate for generation of rotational constants which were measured in the case of 1,2-difluoroethane as ground-state (B_0) values. Accordingly, our refinements were carried out on models defined by the r_α set of geometrically consistent distances related to the electron-diffraction r_a set and the spectroscopic $r_z = r_\alpha{}^\circ$ set by[16]

$$r_a{}^T = r_\alpha{}^T + \delta r^T + K^T - (l^2)^T/r_\alpha \tag{5}$$

and

$$r_z = r_\alpha{}^T - (3/2)a_3[(l^2)^T - (l^2)^0] + K^T - K^0 \tag{6}$$

Here δr is a correction for the effect of centrifugal distortion, K is a correction for motion perpendicular to the internuclear line (perpendicular amplitude), l is the overall amplitude of vibration, and a_3 is the Morse function anharmonicity constant; the superscripts designate temperatures. Values of δr, K, some of the l's, and $\alpha_s{}^{har}$ (see eq 7) were first calculated from a symmetrized force field which reproduced the fundamentals assigned[6] to the gauche conformer to within 1%. (This approximate force field together with the definitions of the symmetry coordinates and wavenumber agreement are given in Table I. We emphasize that the force field has no special virtue; it is reasonable, however, and satisfactory for our purposes because the quantities derived from it are not very sensitive to small changes.) The r_z bond lengths calculated from eq 5 were then used with the angle parameters to generate rotational constants $B_z = 505379$ MHz·u·Å$^2/I_z$ for comparison with values obtained from the observed B_0 according to

$$B_z = B_0 + \sum_s \alpha_s{}^{har}/2 \tag{7}$$

The r_a values necessary for eq 1 were obtained from the r_α values according to eq 5; the r_α values were generated from the r_α bond lengths and angle parameters.

All of the correction terms in eq 5 and 6 are torsion angle

Table II. Summary of Structural Results[a,b] from Refinements of Different Models[c] of 1,2-Difluoroethane

	22 °C			203 °C			420 °C				Van Schaick
	2C	2S	CP	2C	2S	CP	2C	2S	CP	Brunvoll[d]	et al.[e]
⟨C-C,F⟩[f]	1.427(2)	1.427(2)	1.427(2)	1.428(2)	1.427(2)	1.427(2)	1.429(2)	1.426(2)	1.426(2)	1.428(7)	1.438
Δ[g]	0.114(3)	0.114(3)	0.114(3)	0.113(3)	0.114(4)	0.112(4)	0.118(3)	0.114(3)	0.115(3)	0.116(14)	0.141
C-H	1.092(4)	1.092(4)	1.092(3)	1.089(4)	1.089(4)	1.088(4)	1.091(3)	1.091(3)	1.091(3)	1.095(10)	1.126(10)
∠CCF	110.3(1)	110.3(1)	110.3(1)	110.2(1)	110.3(1)	110.3(1)	110.2(1)	110.4(1)	110.4(1)	110.3(20)	108.3(1)
∠CCH	109.9(11)	110.4(11)	111.0(10)	111.3(12)	111.6(12)	111.8(11)	109.7(17)	110.1(20)	110.6(16)		108.3(8)
∠HCH	109.6(16)	109.2(16)	108.5(16)	109.3(20)	108.6(19)	107.8(19)	112.7(24)	109.8(25)	109.5(23)		
∠FCH	108.5(9)	108.2(9)	107.9(8)	107.2(8)	107.3(9)	107.4(7)	107.2(10)	108.2(12)	107.8(9)		
∠FCCF	108.5(2)	108.6(3)	108.7(17)	108.8(2)	108.8(2)	108.8(15)	108.8(3)	108.7(4)	108.8(15)	110.6(70)	105.7(3)
% trans	5.6(38)	3.3(50)	4.0(18)	9.1(46)	9.2(56)	10.3(24)	13.9(48)	22.7(55)	19.4(29)		
σ(g)[a]		13.1(8)			18.2(14)			26.3(30)			
σ(t)[a]		[20.3][h]			[25.8][h]			[31.2][h]			
V_1			0.82(94)			0.62(76)			0.64(61)		
V_2			−2.77 (39)			−2.64(43)			−2.02(48)		
V_3			2.48(47)			2.28(47)			1.84(49)		
R[i]	0.0728	0.0776	0.0754	0.0732	0.0749	0.0744	0.0599	0.0579	0.0558		

[a] Distances (r_α) in ångstroms, angles and root mean square torsional amplitudes (σ) in degrees, torsional potential coefficients (V) in kilocalories per mole; g and t refer to gauche and trans conformers. [b] Parenthesized numbers are twice estimated standard deviations. [c] 2C, 2S, and CP are respectively "two-conformer", "double-σ", and "cosine potential" models. See text. [d] Reference 3. Values of ⟨C-C,F⟩ and Δ were calculated from distances given. [e] Reference 4. Values of ⟨C-C,F⟩ and Δ were calculated from distances given. [f] $[r(\text{C-C}) + 2r(\text{C-F})]/3$. [g] $r(\text{C-C}) - r(\text{C-F})$. [h] Assumed, [i] $R = [\Sigma w_i\Delta_i^2/\Sigma w_i(s_iI_i(\text{obsd}))^2]^{1/2}$ where $\Delta_i = s_iI_i(\text{obsd}) - s_iI_i(\text{calcd})$.

Table III. Interatomic Distances in 1,2-Difluoroethane from Different Models[a]

	r_a/Å[b]			$(r_a - r_\alpha)^c$ ×10⁴/Å	$(r_a - r_g)^c$ ×10⁴/Å	$(r_\alpha - r_z)$ ×10⁴/Å
	2C	2S	CP			
			22 °C			
C-H	1.103(4)	1.103(4)	1.103(4)	112	−52	−8
C-F	1.389(2)	1.389(2)	1.389(2)	0	−20	−3
C-C	1.503(3)	1.503(3)	1.503(3)	1	−26	−3
H·H	1.793(22)	1.788(22)	1.780(22)	80	−92	
F·H	2.023(10)	2.019(11)	2.017(9)	23	−56	
C·H	2.141(13)	2.148(14)	2.155(12)	33	−57	
C·F	2.374(3)	2.374(3)	2.374(3)	−3	−20	
F··F(g)	2.895(4)	2.899(4)	2.898(15)	−41	−59	
F_2··H_8(g)	2.552(18)	2.564(18)	2.574(21)	−21	−91	
F_2··H_7(g)	3.309(10)	3.310(10)	3.314(17)	29	−28	
F··F(t)	3.589(4)	3.588(4)	3.588(8)	4	−9	
F··H(t)	2.640(18)	2.650(19)	2.657(17)	−32	−90	
			203 °C			
C-H	1.102(4)	1.102(4)	1.102(4)	133	−52	−29
C-F	1.390(2)	1.390(2)	1.390(2)	5	−22	−5
C-C	1.504(3)	1.503(3)	1.502(3)	7	−29	−4
H·H	1.787(25)	1.779(24)	1.769(25)	99	−94	
F·H	2.007(10)	2.007(11)	2.009(9)	34	−58	
C·H	2.158(15)	2.162(15)	2.162(13)	54	−55	
C·F	2.374(3)	2.374(3)	2.373(3)	2	−25	
F··F(g)	2.888(4)	2.896(4)	2.897(15)	−79	−108	
F_2··H_7(g)	2.567(22)	2.580(21)	2.584(22)	−42	−132	
F_2··H_8(g)	3.320(10)	3.318(10)	3.317(17)	33	−39	
F··F(t)	3.589(4)	3.588(4)	3.588(7)	3	−18	
F··H(t)	2.662(19)	2.668(19)	2.667(17)	−61	−131	
			420 °C			
C-H	1.109(3)	1.109(3)	1.109(3)	174	−46	−63
C-F	1.390(2)	1.389(2)	1.389(2)	12	−24	−5
C-C	1.508(3)	1.504(3)	1.505(3)	19	−28	−1
H·H	1.831(27)	1.799(30)	1.796(27)	133	−101	
F·H	2.009(13)	2.021(15)	2.016(12)	55	−58	
C·H	2.144(20)	2.145(24)	2.153(19)	79	−57	
C·F	2.374(3)	2.375(3)	2.375(3)	6	−31	
F··F(g)	2.882(5)	2.900(5)	2.899(12)	−120	−161	
F_2··H_7(g)	2.531(29)	2.560(33)	2.568(27)	−63	−179	
F_2··H_8(g)	3.310(13)	3.307(16)	3.312(17)	42	−49	
F··F(t)	3.588(4)	3.588(4)	3.588(6)	5	−26	
F··H(t)	2.644(25)	2.645(29)	2.654(23)	−91	−179	

[a] See footnote *c*, Table II, and text. [b] The symbol types X-Y, X·Y, and X··Y respectively refer to bonds, geminal distances, and vicinal distances. [c] The amplitude values involved in these corrections are those listed in Table IV.

sensitive and in the 2S and CP models appropriate values of each were given to each pseudoconformer. Some of the centrifugal distortion corrections δr, usually negligible at room temperature, can attain rather large values at elevated tem-

Table IV. Amplitude Results[a,b] for Different Models[c] of 1,2-Difluoroethane

	22 °C			203 °C			420 °C		
	2C	2S	CP	2C	2S	CP	2C	2S	CP
C–H	0.076(5)	0.075(5)	0.075(5)	0.074(4)	0.074(4)	0.074(4)	0.070(4)	0.069(4)	0.069(4)
C–F	0.053(3)	0.053(3)	0.053(3)	0.056(3)	0.056(3)	0.055(3)	0.057(3)	0.057(3)	0.057(3)
C–C	0.063(8)	0.062(9)	0.062(9)	0.066(9)	0.067(9)	0.064(9)	0.066(8)	0.065(8)	0.064(8)
H·H	[0.128]	[0.128]	[0.128]	[0.130]	[0.130]	[0.130]	[0.134]	[0.134]	[0.134]
F·H	0.107 } (9)	0.106 } (10)	0.101 } (10)	0.110 } (11)	0.110 } (11)	0.109 } (11)	0.117 } (12)	0.117 } (12)	0.113 } (11)
C·H	0.111	0.110	0.106	0.111	0.110	0.114	0.121	0.123	0.119
C·F	0.069(3)	0.069(3)	0.069(3)	0.078(4)	0.078(4)	0.078(4)	0.087(4)	0.087(4)	0.087(4)
F··F(g)	0.131 } (9)	[0.056	[0.056	0.175 } (15)	[0.068	[0.068	0.210 } (22)	[0.079	[0.079
F_2··H_8(g)	0.153	0.158	0.158	0.184	0.176	0.176	0.209	0.200	0.200
F_2··H_7(g)	0.096	0.106	0.106	0.112	0.112	0.112	0.121	0.121	0.121
F··F(t)	0.057	0.068	0.068	0.078	0.079	0.079	0.091	0.092	0.092
F··H(t)	0.154	0.141]	0.141]	0.186	0.154]	0.154]	0.213	0.172]	0.172]

[a] Amplitudes in ångstroms. [b] Parenthesized values are twice estimated standard deviations; quantities without parenthesized error estimates were calculated from the force field of Table I; bracketed quantities were refined as a group. [c] 2C, 2S, and CP are respectively "two-conformer", "double-σ", and "cosine potential" models; see text.

Table V. Correlation Matrix (×100) for CP Model at 22 °C

	⟨C–C,F⟩[a]	Δ[b]	r_{C-H}	∠CCF	∠CCH	∠HCH	V_1	V_2	V_3	l_{C-F}	l_{C-H}	l_{C-C}	$l_{F\cdot H}$	$l_{C\cdot F}$
σ_{LS}[c]	0.038	0.112	0.128	3.14	34.8	57.2	33.2	13.6	16.7	0.093	0.126	0.282	0.304	0.068
	100	35	−21	−92	−5	61	−14	−12	−6	27	4	35	−14	23
		100	−1	−52	−3	18	−7	−7	2	−51	24	−56	−6	−12
			100	34	−22	47	−3	4	−2	−18	−1	−19	−1	−7
				100	−20	−34	12	11	3	−12	−10	−18	27	−14
					100	−65	−2	8	3	5	2	3	−65	−12
						100	−11	−10	−8	13	−1	19	22	20
							100	46	85	−7	−2	−6	0	−6
								100	−7	8	−6	5	−4	2
									100	−14	2	−12	−6	−10
										100	−36	92	−2	49
											100	−28	1	−15
												100	−6	42
													100	20
														100

[a] [r(C–C) + 2r(C–F)]/3. [b] r(C–C) − r(C–F). [c] Standard deviation from least squares. Distances and amplitudes in ångstroms, angles in degrees, potential constants in kcal/mol.

peratures (e.g., ~0.0036 Å for r(F···F) in gauche 1,2-difluoroethane at 421 °C). Careful work requires attention to this fact.

Geometrical parameters common to the three models were the distances and bond angles ⟨C–C,F⟩ = [r(C–C) + 2r(C–F)]/3,Δ = r(C–C) − r(C–F), r(C–H), ∠CCF, ∠CCH, and ∠HCH. In addition, for the 2C model the gauche torsion angle ∠FCCF and the composition were required; for the 2S model ∠FCCF, the composition, and the root mean square torsional amplitudes of the gauche and trans conformers σ_g and σ_t; and for the CP model the coefficients V_1, V_2, and V_3 in the three-term cosine potential function. All distances except vicinal H··H were included. For the 2S model each torsion-sensitive distance was represented by nine terms as described in the preceding section, and for the CP model amplitudes were refined individually or in groups with differences between members set to values calculated from the force field; some amplitudes were found to be unrefinable and were given the calculated values. For the 2C model, these groups are evident from Table IV, but the natures of the 2S and CP models make this torsion-sensitive amplitude harder to present: the values in the table are the *lead frame* amplitudes, i.e., those corresponding to the terms for the pseudoconformers at the minima of the potential.

Final Model

The results of several of the many structure refinements together with results from the earlier investigations[3,4] are presented in Tables II–IV. Our results correspond to the "best models" of each type at each of the experimental temperatures. They provide a fit to within 0.1 MHz of the observed rotational constants (A_o = 17322.4, B_o = 5013.1, C_o = 4382.8)[11] as converted (A_z = 17303.5, B_z = 5003.2, C_z = 4379.6) Incidentally, refinements carried out without inclusion of the rotational constants led to parameter values insignificantly different from those of the best models. The diffraction and microwave data are thus indicated to be completely consistent.

The values of the quality-of-fit factor R given in Table II are essentially equal for all model types at each temperature, although at the highest temperature R is least for CP and at the lowest temperature least for 2C. The contents of Tables II–IV show further that the three model types have essentially the same values at each temperature for those parameters common to all. The selection of final model then comes down to which represents best the effects of torsion. Both the 2S and CP models are in this respect preferable to the 2C, which contains no specific representation of torsional properties. Our choice of CP over 2S is somewhat arbitrary, but is consistent with our past experience in the analysis of similar torsional problems in other molecules, particularly at high temperatures. We emphasize that this choice does not lead to conclusions about torsion-related properties incompatible with those derived from other models: as will become clear from later discussion, the values of each of these properties derived from the three models have ranges of uncertainty which overlap comfortably. Table V is the correlation matrix for the CP model at 22 °C; the others are similar.

Results and Discussion

The angle- and bond-length values of Tables II and III are pleasingly constant from one temperature to the next. (Actu-

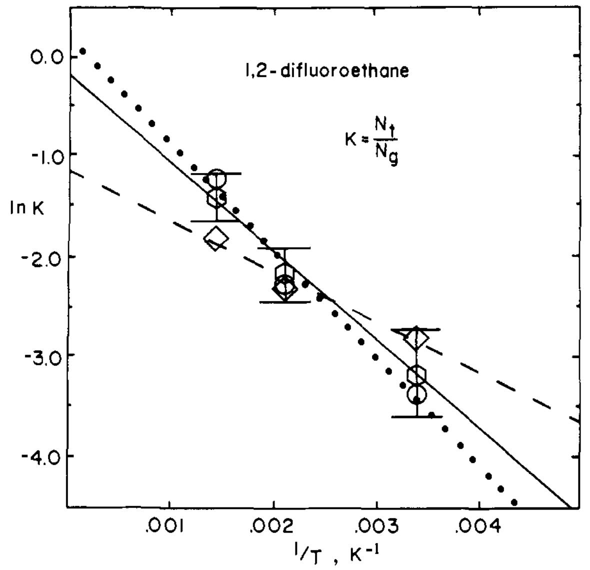
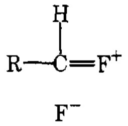


Figure 4. van't Hoff plots of the gauche–trans compositions. Open circles are from the 2S model, hexagons from the CP, and diamonds from the 2C. The dotted, solid, and dashed lines are least-square fits to these data.

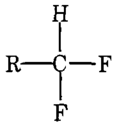
ally only the r_z values are temperature independent, but the effect of temperature on the r_a, r_g, and r_α types is very small.) The nearly identical structures obtained from the three independent experiments are strong evidence for the accuracy of the parameter values and for the accuracy of Brunvoll's earlier results with which they are in excellent agreement. Kveseth's recent results,[9] too, are in excellent agreement with ours and Brunvoll's. We thus conclude that to the extent that the results of Van Schaick et al.[4] differ significantly from those obtained in the other investigations, they must be regarded as in error. We turn now to some specific points of interest.

Bond Lengths. The C–F and C–C bond lengths in the symmetrically substituted fluoroethanes show interesting trends which are suggestive of systematic differences in bonding. In the series 1,2-difluoroethane, 1,1,2,2-tetrafluoroethane,[17] and hexafluoroethane,[18] the C–F bond lengths are respectively 1.389 (r_a), 1.350 (r_a), and 1.326 Å (r_g); the C–C bonds are 1.503 (r_a), 1.518 (r_a), and 1.545 Å (r_g). The progressive shortening of the C–F bond in this series of compounds is similar to that observed in the fluorinated methanes.[19] As in the methanes this shortening may be attributed[19] to partial double-bond character arising from resonance structures of type I which have little importance for molecules having only one fluorine atom on a carbon, but play an increasingly important role as the number of attached fluorines increases. The lengthening of the C–C bond throughout the fluoroethane series may be taken to reflect increasing Coulomb repulsions between the carbon atoms arising from the positive charges deposited upon them by the highly polar character of the C–F bonds. Crude estimates of these electronic charges based upon bond moments of 0.3 and 1.5 D for C–H and C–F[20] are −0.05, −0.40, and −0.69 for the di-, tetra-, and hexafluoro compounds. The corresponding value for ethane itself is +0.18 and in this simple picture the C–C bond length is predicted to lie between those of 1,2-difluoroethane and 1,1,2,2-tetrafluoroethane; at r_a = 1.532 Å[21] (calculated from published r_g) it is actually intermediate between those of the tetrafluoro and hexafluoro compounds.



$$\mathrm{R{-}\overset{\displaystyle H}{\underset{\displaystyle F^-}{C}}{=}F^+}$$

I



$$\mathrm{R{-}\overset{\displaystyle H}{\underset{\displaystyle F}{C}}{-}F}$$

II

Relative Stabilities of the Gauche and Trans Forms. The greater stability of the gauche form of 1,2-difluoroethane stands in puzzling contrast to the greater stability of the trans form in the other 1,2-dihaloethanes. The latter circumstance can be regarded as the consequence of both steric and static charge effects, the charge effects of course leading to mutual repulsion of symmetry-related atoms. The puzzle in the case of 1,2-difluoroethane arises from the presumption that these charge effects are even greater for it than for the other 1,2-dihaloethanes because the polarity of the C–F bond is greater than those of C–Cl, C–Br, and C–I. A significant attractive interaction between the fluorine atoms is thus suggested.

The situation just described is not unique to 1,2-difluoroethane: the gauche conformation appears to be the more stable in many structurally similar molecules, both organic and inorganic, containing pairs of electronegative atoms or highly polar bonds. This has been termed[22] the "gauche effect" and is analogous to a similar phenomenon, the "cis effect", which operates in molecules such as the substituted ethylenes.[23,24] Explanations for the preferred gauche or cis conformations differ in details which are best obtained from the original articles[22-25] and references cited therein. It is sufficient to say here that the predominance of a conformation is a result of competitive terms, often delicately balanced, in the energies of the systems. Thus, ab initio quantum mechanical calculations for 1,2-difluoroethane at the double ζ[26] and 4-31G[27] levels, respectively with and without geometry optimization, predict the trans from to be the more stable, whereas a recent INDO calculation[28] (a report which also addresses the gauche effect) predicts the gauche to be the more stable. An alternative view of the conformational problem is provided by the results of molecular-mechanics calculations on molecules similar to 1,2-difluoroethane. For example, when the total energy of these molecules is regarded as the sum of an electrostatic term consisting of dipole–dipole interaction energies and a "steric" term consisting of the energies of stretching, bending, torsion, nonbond interactions, etc.,[28] it is found[29] that the dielectric constant appearing in the electrostatic term must assume a value of ~4 in order to agree.

Energy and Entropy Differences of the Conformers. The effect of temperature on the conformational equilibrium affords a ready means of estimating the energy and entropy differences of the two forms for the 2C and 2S models. For these cases the usual formula

$$N_t/N_g = \tfrac{1}{2}e^{-\Delta S°/R}e^{-\Delta E°/RT} \qquad (8)$$

applies, where N_g and N_t are proportional to the fractions of gauche and trans molecules in the sample and the factor ½ is the ratio of their statistical weights. Figure 4 shows the experimental points plotted in the usual van't Hoff form together with least-squares curves fitted to them. The CP model does not lend itself quite so easily to a determination of the energy and entropy differences because the sample composition is not included specifically as a parameter. To obtain a rough estimate of the relative amounts of the two forms the values of V_1, V_2, and V_3 obtained from the refinements of the CP model at the three experimental temperatures (Table II) were used with eq 3 to generate the distribution of molecules along the torsional coordinate. If one somewhat arbitrarily takes the maxima of the potential functions as boundaries for definitions of gauche and trans molecules, one calculates from eq 3 sample compositions with standard deviations corresponding to 4.0 (18), 10.3 (24), and 19.4 (29)% trans at 22, 203, and 420 °C, respectively. These results and the least-squares fit to them are also shown in Figure 4. The energy differences $\Delta E° = E_t° - E_g°$ and entropy differences $\Delta S° = S_t° - S_g°$ obtained from the slopes and intercepts of the van't Hoff plots in Figure 4 are listed in Table VI. (We note that $\Delta E°$ for the CP model obtained by this method is pleasingly close to the value 1.64

Table VI. Energy and Entropy Differences,[a] Torsional Potential Constants and Frequencies, and Rotational Barriers for Conformers of 1,2-Difluoroethane

model type	this work[b] 2C	2S	CP	HHK[c]	H-WG[d]
$E_t° - E_g°$, kcal/mol	0.99(0.81)	2.12(1.10)	1.76(0.51)[e]	1.98 ± 0.08	0.60 ± 0.15
$S_t° - S_g°$, cal mol^{-1} K^{-1}	−0.94(1.68)	1.71(2.06)	0.97(0.96)		0.52[f]
V_1, kcal/mol	1.09(0.77)	−0.31(1.03)	0.67(0.42)	−2.92[g]	3.00
V_2, kcal/mol	−2.11(1.17)	−2.27(1.58)	−2.53(0.25)	0.41[g]	−3.12
V_3, kcal/mol	2.14(0.95)	1.47(1.18)	2.21(0.28)	2.25[g]	3.55
ω_g, cm^{-1}	123(5)	111(5)	128(6)	148[h]	147[h]
ω_t, cm^{-1}	90(37)	51(82)	84(11)	117-93[i]	117-102[j]
t-g barrier, kcal/mol	0.95(2.24)	0.15(1.69)	0.72(0.45)	1.86	2.56
g-g barrier, kcal/mol	4.22(1.47)	3.28(1.91)	4.52(0.72)	1.34	7.07

[a] Parenthesized quantities are estimated 2σ. [b] 2C, 2S, and CP are respectively a simple two-conformer model, a two-conformer model including torsional motions as a special parameter, and a model based on a three-term cosine potential for torsion. [c] Reference 6. [d] Reference 5b. [e] Value from van't Hoff plot. Value calculated from $V(\phi)$ equals 1.64 kcal/mol. See text. [f] At 300 K. [g] A "composite" potential. Two other potentials are also discussed. [h] 1 ← 0 transition. [i] Five transitions. [j] Four transitions.

kcal/mol calculated from the potential function.) Although these energy and entropy differences are rather different for the three models, they are not inconsistent when account is taken of the listed uncertainties. Our preferred model CP has an energy difference close to the spectroscopic value 1.98 ± 0.08 kcal/mol of Harris et al.,[6] derived from liquid-phase data, but is rather larger than Huber-Wälchli and Günthard's[5] gas value of 0.6 kcal/mol. The value in the gas should presumably be smaller than that in the liquid (by the difference in the enthalpies of vaporization of the two conformers), but any estimate of the magnitude of this difference is quite uncertain.

Torsional Potentials, Barriers, and Vibrational Frequencies. The electron-diffraction results for the three models allow one to calculate crude torsional potential functions and correspondingly to make rough estimates of rotational barriers and torsional frequenices. The potential for the CP model is defined by the values of the V_i obtained directly from the structure refinements. For the 2S and 2C models we used the method previously described,[30] appropriately modified to take account of the gauche instead of the trans conformer as the lower energy form, to obtain these quantities. This method requires that the torsional potential (eq 4) reproduce the measured values of $E_g° - E_t°$, ∠FCCF(g), and the curvature of the gauche minimum (k_ϕ). Because the last item was not a parameter in the 2C model, it was estimated from $l(\mathrm{F{\cdot\cdot}F})_g$ by first subtracting the contribution of the "frame" amplitudes as calculated from the force field and then converting the result to ⟨FCCF(g)⟩ through the known angle-distance dependence. Figure 5 shows the potential functions for the three models. As indicated above, they are not inconsistent when account is taken of the associated uncertainties. Clearly, however, the 2S curve is inconsistent with the assumption that the force constants for the torsion of the gauche and trans species are equal: the curvatures of the function are quite different in the regions of the minima.

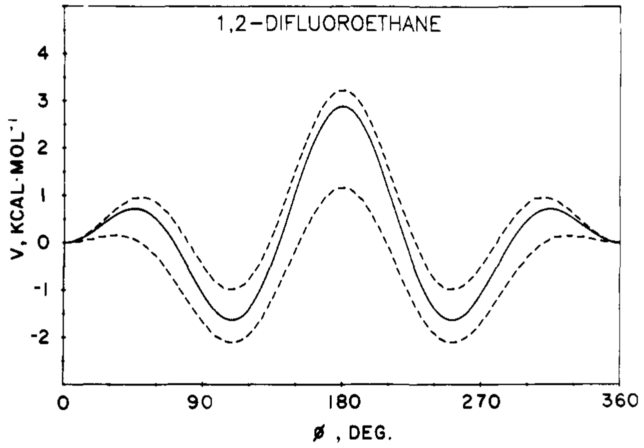


Figure 5. Curves of the torsional potentials. The trans conformation is at $\phi = 0$. Upper, middle, and lower curves are respectively from the 2C, CP, and 2S models.

The torsional barriers are listed in Table VI with uncertainties derived from the uncertainties in the V_i. In a strict sense the potential for the CP model should probably be regarded as a free-energy function $G(\phi)$ and hence be temperature dependent. We see no evidence of this temperature dependence, however (Table II), and have ignored it. The barriers appear to be less model dependent than the energy and entropy differences. Estimates of the torsional frequencies were made from the harmonic approximation $\omega = (2\pi c)^{-1}(k_\phi/\mu_1)^{1/2}$ where k_ϕ equals $d^2V/d\phi^2$ evaluated at the gauche and trans angles and μ_1 is the reduced moment of inertia taken to be equal to the matrix element G_ϕ^{-1} obtained in the course of our force-field calculations. The results of these calculations are summarized in Table VI. The value 128 cm^{-1} for the gauche conformer calculated from our preferred model CP is in reasonable agreement with the value 148 cm^{-1} attributed to the 1 ← 0 transition. Our value of 84 cm^{-1} for the trans conformer is rather lower than the range of transitions 117-93 cm^{-1} suggested[6] as possibly arising from this mode.

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Supplementary Material Available: Tables of total intensities and final backgrounds at all temperatures, and figures of intensity curves and backgrounds from the 203 and 420 °C experiments (30 pages). Ordering information is given on any current masthead page.

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Energy Transfer in Ion–Molecule Association Reactions. Dependence of Collisional Stabilization Efficiency on the Collision Gas

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Abstract: The energized proton-bound dimer of $(CH_3)_3N$ is formed by reaction of $(CH_3)_3NH^+$ with $(CH_3)_3N$. Energy transfer from the energized dimer is accomplished by a variety of collision gases and relative per collision stabilization efficiencies, β, are obtained. There is a positive correlation of β with the dipole moment of the collision gas but no correlation with the reduced mass of the colliding pair (proportional to the "fly-by time" of the collision), to the polarizability of the neutral, or to the number of transitional modes of the collision pair. Comparisons are made with data of other workers on both ionic and neutral systems. A long-range rotational–rotational energy transfer mechanism is suggested.

Introduction

A great deal of both experimental and theoretical work has been devoted to the study of energy transfer in vibrationally excited molecules. Almost all this work has been done on neutral systems, and is generally discussed in terms of unimolecular reaction rate theory.[1] Tardy and Rabinovitch have given a very thorough review of this topic for neutral–neutral systems.[2]

Studies of energy transfer in thermal ion–molecule reactions are much less common. Harrison has reviewed the early work in this area.[3] Systematic studies using a variety of collision gases are rarer still. The first such study was reported by Anicich and Bowers,[4] where the effects of various third-body gases were measured in the stabilization of dimers of 1,1-difluoroethylene and benzene. Miasek and Harrison have done a similar study of the collisional deactivation of $(C_5H_9^+)^*$.[5] We now present a study of the effects of 22 inert gases in the dimerization of trimethylamine. This study was intended to test the validity of the assumption of unit stabilization efficiency for all stabilizers that has been used in all theoretical models of association reactions. We have attempted to determine which molecular parameters are important in determining this efficiency. Neilson et al. have presented a complete experimental study of the dimerization of pure trimethylamine[6] and Bass et al. have developed a theoretical model of the system based on statistical theory.[7]

Kinetic Analysis

The general mechanism is of the type

$$AH^+ + A \xrightarrow{k_2} A_2H^+ \qquad (1)$$

$$d[A_2H^+]/dt = k_2[AH^+][A] \qquad (2)$$

where k_2 is, in general, pressure dependent. A more detailed mechanism which has been applied to a number of ion–molecule systems is[4,7]

$$AH^+ + A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} (A_2H^+)^* \qquad (3)$$

$$(A_2H^+)^* + A \xrightarrow{k_s} A_2H^+ + A \qquad (4)$$

$$(A_2H^+)^* + M \xrightarrow{k'_s} A_2H^+ + M \qquad (5)$$

where the asterisk indicates that the molecule is in some rotationally and/or vibrationally excited state. This mechanism yields

$$d[A_2H^+]/dt = (k_s[A] + k'_s[M])[A_2H^+]^* \qquad (6)$$

Making a steady-state approximation for $[A_2H^+]^*$ and substituting into eq 6 gives an expression for $d[A_2H^+]/dt$ that may be equated with eq 2 and solved for k_2. The resulting expression is

$$k_2 = \frac{k_f k_s[A] + k_f k'_s[M]}{k_b + k_s[A] + k'_s[M]} \qquad (7)$$

From eq 7, it may easily be seen that, in the limit as both A and M approach zero

$$dk_2/d[M] = k_f k'_s/k_b \equiv k_{3,M} \qquad (8)$$

$$dk_2/d[A] = k_f k_s/k_b \equiv k_{3,A} \qquad (9)$$

Thus, assuming that k_f and k_b are constant, the ratio of $k_{3,M}$ to $k_{3,A}$ gives the desired result:

$$k_{3,M}/k_{3,A} = k'_s/k_s \qquad (10)$$

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