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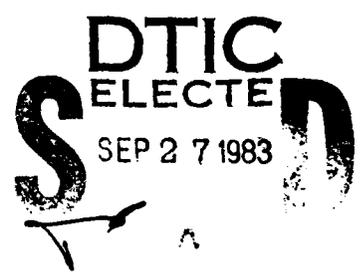
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WHEN IS AN INTERNAL ROTATION A VIBRATION?

Lt Christopher Lisanti
Captain Larry P. Davis
Lt Mavis Compagno

Project 2303



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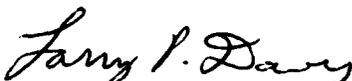
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Larry P. Davis
Project Scientist


Armand A. Fannin, Jr, Lt Col
Director, Chemical Sciences


Kenneth E. Siegenthaler, Lt Colonel
Chief Scientist

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Directorate of Chemical Sciences
The Frank J. Seiler Research Laboratory
Air Force Systems Command
United States Air Force Academy
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ABSTRACT

Calculation of entropies for molecules having internal rotations are in error if these rotations are treated as vibrations. Using MNDO-calculated geometries, entropies of a set of molecules were calculated assuming all internal motions were vibrations. Errors were determined for these molecules, with particular attention paid to the ones containing internal rotations.

Based on the total internal partition functions calculated in this manner compared to total internal partition functions calculated by assuming a free rotor for the internal rotation we developed a criterion for determining when the free rotor correction needs to be made to the entropy values. The correction greatly improves the calculated entropy values for molecules with internal rotation.

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CHAPTER 1

INTRODUCTION

The MNDO (Modified Neglect of Diatomic Overlap) computer program developed by Professor Michael J. S. Dewar, University of Texas at Austin, can be used to calculate vibrational frequencies, thermodynamic quantities, when coupled with appropriate statistical mechanics, and the optimized geometries of molecules. While MNDO calculations are fairly representative of most experimental entropy (S^0) values,¹ whenever there are free or slightly hindered internal rotations (such as a methyl rotor adjacent to a triple bond), the MNDO program produces slightly erroneous entropy values at 298.15 K for many of these molecules. Since the calculated entropy values are important for determining a variety of other values, the desire for a higher degree of accuracy is obvious.

A considerable amount of research has already been done on internal rotational barriers and methods of modeling them in various molecules. Professor Dewar and associates have written many articles about the results obtained from MNDO and its predecessor, MINDO/3. Some of these results include the computer-generated optimized geometry of molecules² and entropy values of molecules without internal rotations.¹ Both the optimized geometry of molecules and the entropy values for the molecules without internal rotations are very close to experimental values.¹ However, in molecules with free or only partially free internal rotations, the basic calculations erroneously model these internal rotations as low frequency vibrations. These low frequency vibrations make the vibrational partition function contribution much larger than it should be, which subsequently results in an incorrect vibrational entropy contribution.

This paper describes one method of correcting MNDO calculations involving molecules with free internal rotations (IR) or partially hindered rotations. It consists basically of removing the spurious vibrational mode's (modes') contributions to the vibrational entropy and partition function values, therefore resulting in a more accurate vibrational entropy contribution. The contribution(s) from this mode(s) are then added back in as free internal rotations. Testing of this method involved twenty molecules: four without internal rotations and 16 with free or partially hindered internal rotations.

CHAPTER 2
CALCULATIONS

BASIC METHOD

First, MNDO was used to calculate the molecule's optimized geometry and thermodynamic properties. The only thermodynamic values that were studied were those computed at 298K. This was accomplished on all of the test molecules. MNDO was run on the VAX 11/780 computers at the United States Air Force Academy.

CORRECTIONS

The entropy values for each of the 16 molecules with free or partially hindered internal rotations were then modified by dividing the MNDO calculated vibrational partition value by the spurious vibrational mode contributions to the partition function. The spurious vibrational mode contributions to the vibrational entropy were then removed from the entropy value. Finally, the spurious contributions to the partition and entropy values were replaced with the corresponding completely free internal rotation values.

The spurious vibrational contributions to the partition function were computed using the following equation:

$$q_{\text{vnth mode}} = 1 / (1 - e^{-v/kT}) \quad (1)^3$$

where $k = 6.95196 \times 10^{-1} \text{ cm}^{-1} \text{ K}^{-1}$ and v is the frequency of the n^{th} mode in cm^{-1} (n ranging from 1 to the number of free IRs). The vibrational contribution to the partition function was then corrected by dividing the MNDO vibration partition value by the product of the spurious vibrational contributions.

The contribution to the internal partition function by the "free" internal rotation was then computed using Equation 2:

$$Q_{\text{Free IR}} = (2.7935/n)(10^{38} I_r T)^{1/2} \quad (2)^4$$

with n representing the symmetry number of the rotating group, I_r being the rotational moment of inertia, and T the temperature (K). Following this calculation, the maximum internal partition value was determined using the equation

$$q_{\text{max}}^i = q^{v^*} \times q^r \times Q_{\text{Free IR}} \quad (3)$$

where q^{v^*} is the corrected vibrational partition value, q^r is the rotational partition value, and $Q_{\text{Free IR}}$ is calculated from Equation 2. This value was determined to be the criterion for free internal rotation corrections, and its importance will be discussed in the next section.

Next, the entropy value must be corrected for the free internal rotations. The general equation for entropy (equation 4) results in an equation for the entropy for free internal rotations (equation 5), which is then reduced to equation 6.

$$S = n R [\ln(q) + T(d\ln(q)/dT)] \quad (4)^3$$

$$S_{\text{Free IR}} = n R [\ln(q^{v^*} + T[n/2.7935)(1/10^{38} I_r T)^{1/2}(2.2935/n)(10^{38} I_r)^{1/2}(1/2)(1/T^{1/2})]] \quad (5)$$

$$S_{\text{Free IR}} = n R (\ln(q) + 0.5) \quad (6)$$

In these equations, S is the entropy, n is the number of moles (assumed to be one for our purposes), R is the ideal gas constant, T is the temperature (K), and q is the partition function value calculated in equation 2. Equation 7 is then used for calculating the specific vibrational mode entropy contributions and it is derived from the general equation for entropy.

$$S_{\text{nth mode}} = NR[\ln(q) + T[(1.4388v_{\text{nth}} * e^{-1.4388vn_{\text{th}}/T}) / (T[1 - e^{-1.4388vn_{\text{th}}/T})]]] \quad (7)$$

The vibrational contribution was then corrected by subtracting out the spurious vibrational contributions to the vibrational entropy. The assumed free internal rotation entropy contribution was then added back in when determining the corrected total entropy value.

CHAPTER 3

RESULTS

In order to test the results of these calculations, the value of +/- 1.0 entropy units (1.0 cal/K) within the experimental value was determined to be acceptable. Table I shows the experimental and MNDO entropy values for all test molecules. It was expected that the MNDO entropy values for molecules which did not have any free or hindered internal rotations would be fairly close to the experimental value, and all four test molecules that met this criteria (methane, ethene, ethyne, and propadiene) were within acceptable limits. However, only six of the remaining sixteen molecules with free or hindered internal rotations were considered acceptable. Five of these the six molecules had free internal rotations that were adjacent to a C-C single bond. Therefore, whenever the free internal rotor is adjacent to a double or triple bond, MNDO calculations are only within acceptable limits in one out of ten molecules. Thus it was concluded that hindered internal rotations, such as those in saturated hydrocarbons, can be modeled as low frequency vibrations with a small degree of inaccuracy, while relatively free internal rotors cannot.

TABLE I

MNDO Entropy Calculations

Molecule	$S^{\text{exp}}(\text{cal/K})^{\text{a}}$	$S^{\text{MNDO}}(\text{cal/K})$	Error (cal/K)
Methane	44.50	44.51	-0.01
Ethene	52.44	52.29	+0.15
Ethyne	47.99	47.05	+0.94
Propadiene	58.30	57.67	+0.63
Ethane	54.85	55.20	-0.35
Propane	64.51	65.45	-0.94
Propene	68.80	65.45	+3.35
Propyne	59.30	58.02	+1.28
n-Butane	74.10	73.44	+0.66
1-Butyne	69.51	74.57	-5.06
2-Butyne	67.71	73.25	-5.54
1-Butene	73.48	76.07	-2.59
cis-2-Butene	71.90	79.52	-7.62
trans-2-Butene	70.86	87.09	-16.23
2-methyl-propane	70.42	71.37	-0.95
2-methyl-propene	70.17	80.47	-10.30
1,2 Butadiene	70.03	70.15	-0.48
1,3 Butadiene	66.62	68.85	-2.23
Methanol	56.80	57.05	-0.25
Ethanal	63.50	66.63	-3.13

^aAll experimental entropy values are from the CRC Handbook of Chemistry and Physics, 48th Ed., (Cleveland, Ohio: Chemical Rubber Co., 1967), p. D-51.

The next important step was to develop a criterion which would determine when the correction for free internal rotations should be used. Since the problem stemmed from internal rotational barriers, an attempt was made to find the solution within these barriers by comparing their values with the errors made. However, after compiling the necessary data, it was discovered that the internal rotational barriers were very difficult to calculate or find experimental data for, sometimes poor in agreement between experimental methods, and poor in correlation to the results (see Table II) Although there was a general rule for when to correct or not to correct using internal rotational barriers (at about 2.0 kcal/mol), this method was discarded because of its difficulty and lack of accurate results.

TABLE II

Entropy Differences and Internal Rotation Barriers

Molecule	S^{CORR}	Error ^{MNDO}	Error ^{CORR}	I.R. Barrier(kcal/mol)
Ethane	55.66	-0.35	-0.81	2.93 ^a
Propane	66.40	-0.94	-1.90	3.57 ^a
Propene	64.63	+3.35	+4.17	1.95 ^a
n-Butane	79.88	+1.28	-5.78	3.25-3.40 ^a (methyl)
1-Butene	77.27	-2.59	3.79	3.16-3.99 ^a
cis-2-Butene	76.69	-7.62	-4.79	0.45 ^a
trans-2-Butene	72.58	-16.23	-1.72	1.95 ^a
2-methyl-propane	74.75	-0.95	-4.33	3.6-3.9 ^a
2-methyl-propene	71.59	-10.30	-1.42	2.12-2.35 ^a
1,2 Butadiene	69.94	-0.48	+0.09	1.59 ^a
1,3 Butadiene	71.25	-2.23	-4.63	2.3-5.0 ^a
Methanol	59.02	-0.25	-2.22	1.07-1.60 ^b
Ethanal	63.54	-3.13	-0.04	1.0-1.15 ^b

^aValues found in Internal Rotation in Molecules, Ed. W.J. Orville-Thomas (New York: John Wiley and Sons, 1974), p. 413-415.

^bValues found in Conformational Analysis, Ernest L. Eliel, (Washington D.C.: American Chemical Society, 1981), p. 140.

The next method studied concerned the ratio between q^i calculated and q^i_{maximum} (See Table III). If the program describes the internal rotation incorrectly as a vibrational frequency which is too low, then it will show up as a ratio that is greater than one. If the internal rotation can be modeled as a low vibrational frequency, such as a hindered internal rotation can, then it will show up as a ratio that is less than one, indicating that the MNDO calculation is within the maximum bonds.

This method worked correctly for 13 of the 16 test molecules, incorrectly for only two, and didn't matter for one molecule (see Table IV). In addition to the high percentage of correct decisions, the average percent deviation from experimental entropy values using this criteria is only 2.52%, while using the correction at all times is 3.92% and the uncorrected MNDO results give a 5.50% deviation.

TABLE III

Internal Partition Function Ratios

Molecule	q^i MNDO	q^i max	q^i ratio	Correction(A/T)
Ethane	1.4486×10^3	3.1651×10^3	0.4577	0.46 A
Propane	4.5528×10^4	1.7666×10^5	0.2577	0.96 A
Propene	7.3482×10^4	6.9547×10^4	1.0566	0.82 A
Propyne	3.7918×10^3	1.2126×10^4	0.3127	0.10 A
n-Butane	4.4937×10^5	2.1572×10^7	0.0208	4.50 A
1-Butyne	2.2538×10^6	7.1291×10^6	0.3161	0.00 A/T
2-Butyne	7.6486×10^5	1.2377×10^5	6.1797	4.66 T
1-Butene	2.8119×10^6	9.5216×10^6	0.2953	1.20 A
cis-2-Butene	1.1264×10^7	6.1673×10^6	1.8264	2.83 T
trans-2-Butene	3.6809×10^8	6.4725×10^5	568.6980	14.51 T
2-methyl-propane	1.7454×10^5	1.5044×10^6	0.1160	3.38 A
2-methyl-propene	1.9828×10^7	5.1678×10^5	38.3684	8.88 T
1,2 Butadiene	2.7893×10^5	2.9513×10^5	0.9451	0.39 T
1,3 Butadiene	1.5139×10^5	7.6343×10^5	0.1983	2.40 T
Methanol	4.3509×10^3	1.1642×10^4	0.3737	1.97 A
Ethanal	1.5498×10^5	5.1427×10^4	3.0136	3.09 T

TABLE IV

Correction Comparisons

Molecule	Ratio	Error ^{MNDO}	ΔZ^{MNDO}	Error ^{CORR}	ΔZ^{CORR}	Error(^q riterion)	$\Delta Z^{\text{(q}^{\text{i}}\text{riterion)}}$
Ethane	0.4577	0.35	0.64	0.81	1.48	0.35	0.64
Propane	0.2577	0.95	1.47	1.90	2.95	0.95	1.47
Propene	1.0566	3.35	4.87	4.17	6.06	4.17	6.06
Propyne	0.3127	1.28	2.16	1.38	2.33	1.28	2.16
n-Butane	0.0208	0.66	0.89	5.78	7.80	0.66	0.89
1-Butyne	0.3161	5.06	7.28	5.06	7.28	5.06	7.28
2-Butyne	6.1797	5.54	8.18	0.88	1.30	0.88	1.30
1-Butene	0.2953	2.59	3.52	3.79	5.16	2.59	3.52
cis-2-Butene	1.8264	7.62	10.60	4.79	6.66	4.79	6.66
trans-2-Butene	568.698	16.23	22.90	1.72	2.43	1.72	2.43
2-methyl-propene	0.1160	0.95	1.35	4.33	6.15	0.95	1.35
2-methyl-propene	38.3684	10.30	14.68	1.42	2.02	1.42	2.02
1,2 Butadiene	0.9451	0.48	0.69	0.09	0.13	0.48	0.69
1,3 Butadiene	0.1983	2.23	3.35	4.63	6.95	2.23	3.35
Methanol	0.3737	0.25	0.44	2.22	3.91	0.25	0.44
<u>Ethanol</u>	3.0136	3.13	4.93	0.04	0.06	0.04	0.06
<u>Average values</u>			5.50		3.92		2.52

CHAPTER 4

RECOMMENDATIONS

There is still more to be accomplished before these results can be incorporated into a program such as MNDO. Since most of the testing was done with hydrocarbons and with free internal rotations which were predominantly methyl groups, it is important to verify this test with different internal rotors, such as NH_2 , halogen, and deuterium substituted methyl groups, etc. If more tests conclude that this correction is accurate and reliable enough, then the results can be incorporated into MNDO. Currently, a stand-alone version of the subroutine THERMO from MNDO with these corrections in it is being used to determine whether the separate internal rotation corrections for the vibrational contribution to entropy should be used or not.

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