

The Vibrational Spectra and Structure of the Aluminum Hydride Ion

Ellis R. Lippincott

Citation: [The Journal of Chemical Physics](#) **17**, 1351 (1949); doi: 10.1063/1.1747190

View online: <http://dx.doi.org/10.1063/1.1747190>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/17/12?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Ternary Hydrides Possessing the Cubic Perovskite Structure. II. Vibration Spectra by the Inelastic Scattering of Cold Neutrons](#)

J. Chem. Phys. **51**, 2915 (1969); 10.1063/1.1672433

[Production of Aluminum Hydride by Hydrogen Ion Bombardment](#)

J. Chem. Phys. **42**, 3984 (1965); 10.1063/1.1695871

[Vibration Frequencies of Some Tetrahedral Hydride Ions](#)

J. Chem. Phys. **29**, 451 (1958); 10.1063/1.1744513

[Vibrational Spectra and Structure of Solid Sulfamic Acid and the Sulfamate Ion](#)

J. Chem. Phys. **26**, 77 (1957); 10.1063/1.1743268

[Vibrational Fine Structure in the Absorption Spectra of Uranyl and Plutonyl Ions in Aqueous Solution](#)

J. Chem. Phys. **17**, 349 (1949); 10.1063/1.1747257



mean of about six runs. The activation energy of the reaction, is in excellent agreement with the bond dissociation energy of C—Br in allyl bromide suggested by Roberts and Skinner.⁷ This value is derived from a measurement of the heat of formation of allyl bromide, together with the heat of formation of the allyl radical as determined by Szwarc⁸ from the pyrolysis of propylene.

Using the Bichowsky and Rossini⁹ data for the heat of formation of CH₃Br and that of Kistiakowsky *et al.* for the C—H bond dissociation energy in CH₄, the value 67.3 kcal. may be arrived at for the C—Br bond dissociation energy in methyl bromide. The difference between the value for methyl bromide and that for allyl bromide is not directly comparable with the quantum-mechanical calculation of the resonance energy of the allyl radical, because of the neglect of the difference in the energies of reorganization of the two radicals.

A fuller account of this work will shortly be presented elsewhere.

¹ Kistiakowsky and Stauffer, *J. Am. Chem. Soc.* **59**, 165 (1937).

² Lessig, *J. Phys. Chem.* **36**, 2225 (1932).

³ Vernon and Daniels, *J. Am. Chem. Soc.* **55**, 922 (1933).

⁴ Fugani and Daniels, *J. Am. Chem. Soc.* **60**, 771 (1938).

⁵ Daniels and Veltman, *J. Chem. Phys.* **7**, 756 (1939).

⁶ Meissner and Schumacher, *Zeits. f. physik. Chemie* **185**, 435 (1940).

⁷ Roberts and Skinner, *Trans. Faraday Soc.* **45**, 339 (1949).

⁸ Szwarc, *J. Chem. Phys.* **17**, 284 (1949).

⁹ Bichowsky and Rossini, *The Thermochemistry of Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

The Vibrational Spectra and Structure of the Aluminum Hydride Ion

ELLIS R. LIPPINCOTT

Department of Chemistry, University of Connecticut, Storrs, Connecticut,
and Spectroscopy Laboratory, Massachusetts Institute of Technology,
Cambridge, Massachusetts

October 28, 1949

THE chemical and physical properties of lithium borohydride (LiBH₄) and lithium aluminum hydride (LiAlH₄) suggest the presence of the BH₄⁻ and AlH₄⁻ ions in their respective crystals.¹⁻³ In order to determine if the AlH₄⁻ ion exists in solution, the infra-red and Raman spectra of a 1.28 M solution of LiAlH₄ in diethyl ether have been studied. The sample of LiAlH₄ used in this work was obtained from the Metal Hydrides Corporation and had a purity of 96 percent. The transparent ether solution was prepared by refluxing the solid with anhydrous ether for several hours followed by decantation after the undissolved solid material had settled to the bottom of the container. Samples were pipetted under anhydrous conditions into Raman tubes and sealed before hydrolysis by atmospheric water vapor occurred. A similar procedure was used in filling the infra-red absorption cells.

The infra-red spectrum of the solution was obtained on a Beckman IR-2 infra-red spectrometer in the region 3μ to 15μ. The absorption peaks of the solute were obtained by subtracting the peaks due to the ether from those of the solution. By this procedure the infra-red spectrum was found to consist of two intense bands, with peaks at 764 and 1740 cm⁻¹. Both bands were broad. No weaker bands were observed although it is conceivable that some could be hidden under ether absorptions. The band at 1740 cm⁻¹ has some asymmetry.

The Raman spectrum was obtained using a three-prism Zeiss instrument with a camera lens of aperture number 4.5. The plate factor at 4500Å was 30Å/mm. The excitation unit has been described elsewhere.⁴ Its main features are six AH2 General Electric lamps, six elliptical reflectors, and a filter cell at the center of which is located a 5 ml Raman tube. The 4358Å mercury line was used for excitation. The 4047Å mercury line was removed using a filter solution of saturated sodium nitrite. Solutions of rhodamine 5D GN extra (0.01 g/l) and praseodymium chloride (1% saturated) were used through a thickness of 1 cm to cut down the continuum above 4358Å. Several Raman spectra were taken on various samples before one sufficiently free of a continuum was

obtained. On the best two plates exposure times of two hours were used. The Raman shifts of the solute were obtained by subtracting those due to ether from those of the solutions. The results are summarized in Table I. The reality of the 769-cm⁻¹ line may be

TABLE I. Raman and infra-red data and assignments for the aluminum hydride ion.

Raman	I	Infra-red	I	Assignment	Symmetry
769	(1)	764	(5)	ν_4	F_2
799	(2)			ν_2	E
1741	(2)	1740	(5)	ν_3	F_2
1790	(3)			ν_1	A_1

questioned because of its intensity and the continuum on the plate, but its coincidence with the broad infra-red band at 764 cm⁻¹ suggests that it is real.

Although rigorous selection rules derived for gases do not necessarily hold for substances in solution, the four Raman and two infra-red bands observed and the coincidence of the infra-red bands with two Raman bands are consistent with a tetrahedral model for the AlH₄⁻ ion in solution. The broadness of the infra-red bands is probably due to the partial splitting of the triply degenerate modes of vibration by liquid forces.

Force constants for the stretching and bending vibrations of the AlH₄⁻ ion have been calculated using a simple valence force model.⁵ The values calculated for k and $k\delta/e^2$ are, respectively, 1.89 and 0.126·10⁶ dynes/cm. Since the valence force model involves two force constants, there are two independent relations between the four frequencies which may be used as checks on the model. Table II gives calculated and observed values for $\lambda_3^2 + \lambda_4^2$

TABLE II. Calculated and observed values for $\lambda_3 + \lambda_4$ and $\nu_3\nu_4/\nu_1\nu_2$ assuming a simple valence force potential.

	Observed	Calculated
$\lambda_3 + \lambda_4$	2.14·10 ⁶ dynes/cm	2.26·10 ⁶ dynes/cm
$\frac{\nu_3\nu_4}{\nu_1\nu_2}$	0.93	0.88

and $\nu_3\nu_4/\nu_1\nu_2$. The agreement is good for a simple valence force model, the percentage error being less than the corresponding error for a number of other tetrahedral molecules and ions.⁶

¹ Schlesinger and Brown, *J. Am. Chem. Soc.* **62**, 3429 (1940).

² Feholts, Bond, and Schlesinger, *J. Am. Chem. Soc.* **69**, 1199 (1947).

³ Smith, *Sci. Progress* **35**, No. 139, 515 (1947).

⁴ Harrison, Lord, and Loofbourov, *Practical Spectroscopy* (Prentice-Hall, Inc., New York, 1948).

⁵ G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), p. 182.

A Note on Temperature and the Recombination Coefficient

N. C. GERSON

Air Force Cambridge Research Laboratories, Cambridge, Massachusetts

November 12, 1949

EQUATIONS of the type

$$\alpha = AT^r,$$

where α = recombination coefficient (cm/sec.),¹ T = temperature (°K), and A = dimensional constant have been postulated on many occasions. In early studies on air, carbon dioxide and hydrogen, Erikson^{2,3} obtained values which indicate that the exponent $-2.5 \leq r \leq -2.2$ when T varies from 90°K to 450°K. However, in Erikson's results, $A \neq$ constant. At about the same period Phillips experimentally found $r = -2.2$ for air at constant pressure in the temperature range from about 80°K to 500°K. At low pressures Thomson and Thomson⁴ theoretically indicate that $r = -3$. On the

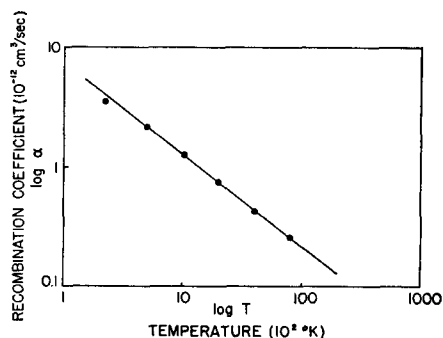


FIG. 1. Plot of α versus T . Amount of oxidation for various concentrations.

basis of statistical equilibrium, Milne⁵ showed that $r = -\frac{1}{2}$ when $T = T_e$, the electron temperature. Similar results were obtained by Tukada,⁶ by Yamonauchi and Kotani⁷ and by Hulbert.⁸ Bates and Massey⁹ indicate that $r = -\frac{1}{2}$ under ionospheric conditions. Thomson found that $r = -5/2$ at low pressures and $r = -\frac{1}{2}$ at high pressures. Loeb⁹ indicates that for ionospheric work, $r = +\frac{1}{2}$.

Amidst the confusion of the above results, it is interesting to note a new value of r which may be obtained from the accompanying figure. Employing data recently computed by Bates and collaborators, a graph of α versus T was plotted. It is readily apparent that in the temperature range 250°K to 8000°K, the value $r = -\frac{1}{2}$ applies. The complete expression obtained from the figure is $\alpha = 2.43 \times 10^{-10} T^{-0.768}$.

¹ Phillips, Proc. Roy. Soc. A133, 246 (1910).

² Erikson, Phil. Mag. 18, 328 (1909).

³ Erikson, Phil. Mag. 23, 747 (1912).

⁴ J. J. Thomson and G. P. Thomson, *Conduction of Electricity Through Gases* (Cambridge University Press, London, 1928), p. 50.

⁵ E. A. Milne, Phil. Mag. 47, 209 (1924).

⁶ T. Tukada, Rept. Radio. Res. Japan 7, 121 (1937).

⁷ T. Yamonauchi and M. Kotani, Proc. Phys. Math. Soc. Japan 22, 61 (1940).

⁸ E. O. Hulbert, *Terrestrial Magnetism and Electricity* (McGraw-Hill Book Company, Inc., New York, 1939), Vol. 8, p. 519.

⁹ D. R. Bates and H. S. W. Massey, Proc. Roy. Soc. A187, 261 (1946).

¹⁰ J. J. Thomson, Phil. Mag. 47, 337 (1924).

¹¹ L. B. Loeb, *Fundamental Processes of Electrical Discharges Through Gases* (John Wiley and Sons, Inc., New York, 1939).

¹² Bates, Buckingham, Massey, and Unwin, Proc. Roy. Soc. A170, 322 (1939).

The Entropy and Configuration of Methylhydrazine

G. J. JANZ AND K. E. RUSSELL

The School of Chemistry and Physics, Pennsylvania State College,
State College, Pennsylvania

October 3, 1949

THE theoretical treatment of Penney and Sutherland¹ indicates that the most stable form of hydrazine should be a skew form as opposed to the symmetrical *trans* configuration. The recent entropy study on this compound by Scott, Oliver, Gross, Hubbard, and Huffman² is in accord with this. The present communication concerns methylhydrazine which is theoretically capable of existing in a *trans* form and two skew forms as shown in Fig. 1. It is possible to investigate the number of forms present by

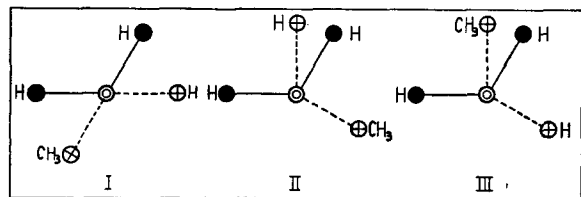


FIG. 1. End-on view of methylhydrazine, I—*Trans*-form, II—"Outer" skew form, III—"Inner" skew form.

a comparison of experimental and calculated entropies of the ideal gas. The results of such an investigation³ together with evidence from dipole moment data are reported in this letter. A summary of the experimental results is given in Table I.

TABLE I.

	E.U./Mole
0–15°K Debye function ($\theta = 193$, six degrees of freedom)	0.073
15–220.79°K (graphical)	18.780
Fusion (2490.5/220.79)	11.279
220.79–298.16°K (graphical)	9.530
Entropy of liquid at 298.16°K	39.662 \pm 0.07
Vaporization (9650.3/298.16)	32.366 \pm 0.11
Entropy of real gas at 298.16°K/49.6 mm.	72.028 \pm 0.18
Entropy of ideal gas	72.036 \pm 0.18
Compression $R \ln(49.6/760)$	–5.423 \pm 0.02
Entropy of ideal gas at 298.16°K/760 mm.	66.61 \pm 0.20

Possible residual entropy at absolute zero has been neglected.⁴ The results of calculations of the entropy from molecular structure and spectroscopic data are given in Table II for an equimolar mixture of the two optical isomers of the "outer" skew form.

TABLE II.

S^0 translational	37.393
S^0 ext. rot.	22.094
S^0 vibrational	1.418
S^0 int. rot. (CH_3 and NH_2)	3.751
S^0 mixing (2 o. isomers)	1.379
Total entropy (ideal gas, 298.16°K/760 mm.)	66.04 e.u.

The vibrational entropy contribution was calculated using an assignment made on the basis of work done by Kahovec and Kohlrusch⁴ and of infra-red and Raman studies in this college. The entropy contributions for restricted internal rotation were taken from the tables of Pitzer and Gwinn,⁵ barriers of 3200 cal./mole for the methyl group (CH_3 vs. NHNH_2) and 3000 cal./mole for the amino group (NH_2 vs. NHCH_3) being taken as best values. The symmetry of the potential energy barrier of the NH_2 group is assumed very nearly a symmetrical threefold cosine-type.^{4, 5} While from stereochemical considerations one would expect the "outer" form to be more stable than the "inner," one would expect a certain percentage of each of the two optical isomers of the "inner" form in the equilibrium mixture. In keeping with this, the experimental and calculated entropies reported above are brought into agreement if methylhydrazine be assumed to consist only of a mixture of 92 mole percent and 8 mole percent of the "outer" and "inner" forms respectively (entropy of mixing, 0.57 e.u.). This result gives a value of E_0 between the "outer" and "inner" forms as calculated from the relationship:

$$E_0 = -RT \ln \frac{N(\text{inner})}{N(\text{outer})} \text{ of about } 1450 \text{ cal./mole.}$$

It is evident that the above conclusions are dependent on the barriers hindering the internal rotation of the methyl and amino groups. Only if the barriers are chosen as 2700 cal./mole and 2050 cal./mole for the methyl and amino hindered rotation respectively (and these are reasonable minimum values corresponding to S^0 int. rot., 4.32 e.u.) does the entropy calculated for the "outer" isomers alone correspond to the calorimetric entropy (i.e., the "inner" and *trans* structures are not allowed). Again if the barriers are 3500 and 3400 cal./mole respectively for the methyl and amino groups (which are probably maximum values, giving S^0 int. rot. as 3.41 e.u.) the calculated entropy is in agreement with the experimental value if methylhydrazine vapor consists of a mixture of 84 mole percent of the "outer" form and 16 mole percent of the "inner" form (entropy of mixing, 0.91 e.u.), the E_0 between these being then about 1000 cal./mole.