

SLOW-NEUTRON SCATTERING AND ROTATIONAL FREEDOM OF METHYL GROUPS IN SEVERAL ORGANIC COMPOUNDS

S.B. HERDADE
INSTITUTO DE ENERGIA ATÔMICA,
SÃO PAULO, BRAZIL

Abstract

SLOW-NEUTRON SCATTERING AND ROTATIONAL FREEDOM OF METHYL GROUPS IN SEVERAL ORGANIC COMPOUNDS. The total cross-sections of CH_3NO_2 , $(\text{CH}_3)_2\text{CO}_2$, $(\text{CH}_3)_2\text{SO}$, $(\text{CH}_3\text{CO})_2\text{O}$, CH_3CH , $(\text{CH}_3)_2\text{SiCl}_2$ and dimethyl polysiloxane (silicone oil) have been measured for neutrons with wavelength λ_n in the range 5 - 10 Å. The scattering cross-sections per H atom, σ_s/H , may be approximated by straight lines $\sigma_s/\text{H} = a_s + b_s \lambda_n$, for $\lambda_n > 5$ Å. An empirical correlation is observed to exist between the slopes b_s and the barrier heights for internal rotation of CH_3 groups in the molecules, and a calibration curve is plotted using some of the experimentally determined slopes and published values of barrier heights determined by other methods. From the slopes 12.3 ± 0.5 b/Å-H for $(\text{CH}_3)_2\text{SiCl}_2$, and 12.3 ± 0.3 b/Å-H for dimethyl polysiloxane, it is concluded that the internal rotation of CH_3 groups in these compounds is practically free. An average barrier height of ~ 1 kcal/mole is estimated for $(\text{CH}_3\text{CO})_2\text{O}$, from the experimentally determined slope 10.8 ± 0.3 b/Å-H.

INTRODUCTION

Total cross-section measurements may be still considered a useful complementary technique to other more advanced methods in the study of the dynamics of hydrogenous groups in molecules by inelastic scattering of slow neutrons [1-4]. For cold neutrons ($E_n \ll 0.025$ eV) the total scattering cross-sections of hydrogenous compounds, as a function of neutron wavelength, can be approximated by straight lines with slopes determined by the inelastic scattering involving an energy gain by the neutrons from the molecules in populated excited states.

The slope of the scattering cross-section per H atom, σ_s/H , of ammonium compounds was found to be a simple function of the barrier for hindered rotation of the NH_4 ion in the crystal [5]. An empirical calibration curve plotted for these compounds has been used to estimate the barrier heights for internal rotation of methylbenzenes [5], on the basis that the CH_3 groups and the NH_4 ion have approximately the same 'effective rotational mass' for neutron scattering.

In the present paper, a new calibration curve is presented for methyl compounds in the range 0 to 3 kcal/mole. This curve is utilized to evaluate the internal rotational freedom of CH_3 groups in acetic anhydride, dimethyl-dichloro-silane, and dimethyl-polysiloxane (silicone oil).

EXPERIMENTAL RESULTS AND DISCUSSION

The total neutron cross-sections of nitromethane, acetone methyl acetate, dimethyl-sulphoxide, acetic anhydride, acetonitrile, dimethyl-dichloro-silane and dimethyl polysiloxane (silicone oil) have been measured

TABLE I. CORRELATION BETWEEN COLD-NEUTRON SCATTERING CROSS-SECTION SLOPES AT ROOM TEMPERATURE (296° K) AND BARRIERS TO INTERNAL ROTATION FOR SEVERAL METHYL COMPOUNDS

Compound	Wavelength range of least-squares fit (\AA)	Scattering cross-section slopes ($b/\text{\AA}-\text{H}$)	Barrier heights from literature (kcal/mole)	Method
CH_3NO_2	6.0 - 8.0	12.9 ± 0.6	0.0063 [9]	μ -wave
$\text{CH}_3\text{C} \equiv \text{CCH}_3$	4.0 - 11.0	12.4 ± 0.3 [3]	< 0.01 [10]	
m-, p-xylene, toluene, mesitylene	4.0 - 11.0	11.4 ± 0.3 [5]	0.190 - 0.540 [11, 12]	Low temperature heat capacity
$(\text{CH}_3)_2\text{CO}$	7.0 - 10.0	11.6 ± 0.3	0.783 [13]	μ -wave
$(\text{CH}_3)_2\text{CO}_2$	7.0 - 10.0	10.6 ± 0.4	1.17 [14]	μ -wave
o-xylene	4.0 - 11.0	9.5 ± 0.3 [5]	1.850 [11]	Low temperature heat capacity
$(\text{CH}_3)_2\text{SO}$	6.0 - 10.0	8.0 ± 0.3	2.9 [15]	μ -wave

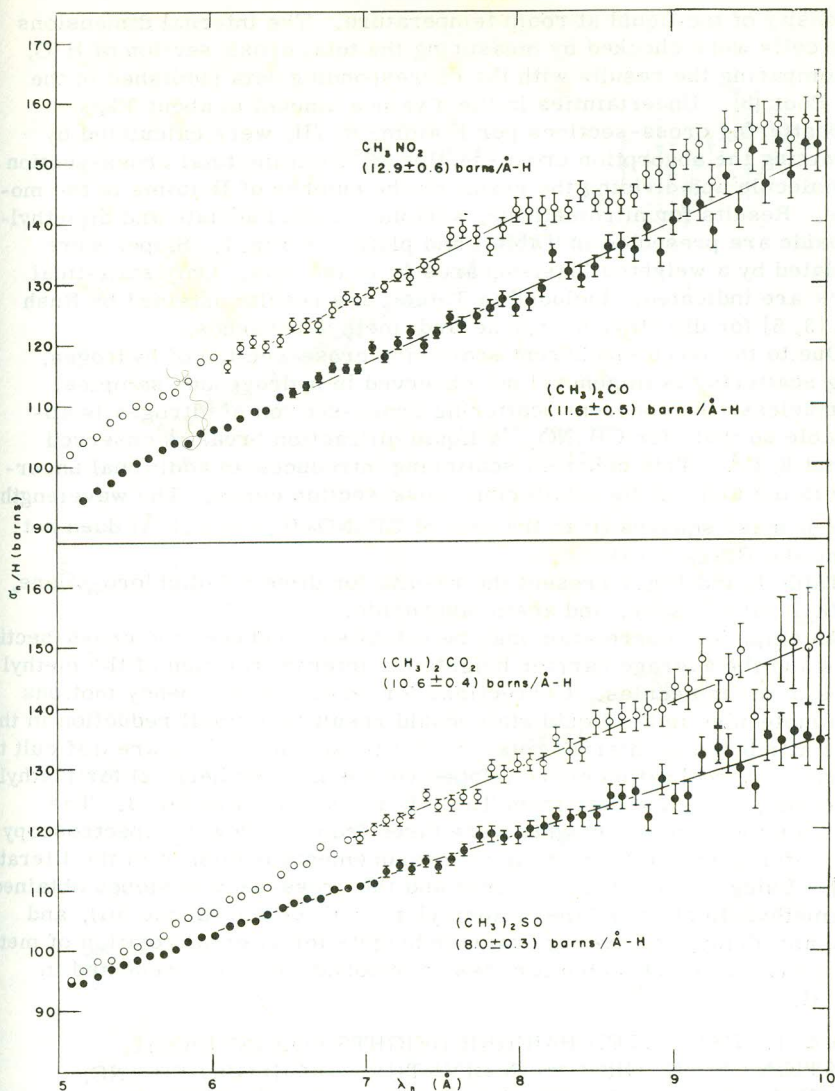


FIG.1. Neutron scattering cross-sections per hydrogen atom of nitromethane, acetone, methyl acetate and dimethyl-sulphoxide in the neutron wavelength range 5 to 10 Å. Slopes were calculated by a weighted least-squares fit to the data. Only statistical errors are indicated.

as a function of neutron wavelength in the range 5 to 10 Å (0.0035 to 0.0008 eV) using a curved slit neutron chopper and time-of-flight spectrometer [6, 7] in operation at the IEA-R1 research reactor. All samples were in the liquid state, at room temperature (296° K) and were contained in aluminium cells such as to present a thickness of 0.25 cm. The number of molecules per square centimetre, n , of each sample has been determined from the measured internal dimensions of the cells and

the density of the liquid at room temperature. The internal dimensions of the cells were checked by measuring the total cross-section of H_2O , and comparing the results with the corresponding data published in the Barn Book [8]. Uncertainties in the n values amount to about 3%.

Scattering cross-sections per H atom, σ_s/H , were calculated by subtracting the absorption cross-section [8] from the total cross-section per molecule and dividing the result by the number of H atoms in the molecule. Results for nitromethane, acetone, methyl acetate and dimethylsulphoxide are presented in Table I and plotted in Fig. 1. Slopes were calculated by a weighted least-squares fit to the data. Only statistical errors are indicated. Included in Table I are results obtained by Rush et al. [3, 5] for dimethyl-acetylene and methyl-benzenes.

Due to the large incoherent scattering cross-section of hydrogen, Bragg scattering is in general not observed in hydrogenous samples. Nevertheless, the coherent scattering cross-section of nitrogen is appreciable so that, for CH_3NO_2 , a liquid diffraction break is observed at about 8.2 Å. This coherent scattering introduces an additional uncertainty in the slope of the scattering cross-section curve. The wavelength range of least-squares fit to the data of CH_3NO_2 (6.0 to 8.0 Å) does not include the Bragg break.

Table II and Fig. 2 present the results for dimethyl-dichloro-silane, dimethyl-polysiloxane, and acetic anhydride.

An empirical correlation may be established between the cross-section slopes and the average barrier heights for internal rotation of the methyl groups in the molecules. Corrections for other low-frequency motions of the molecules in the liquid state would result in a small reduction in the slopes attributed to internal rotation, but these corrections are difficult to estimate. A calibration curve (slopes versus barrier heights) for methyl compounds, using the data from Table I, is presented in Fig. 3. The values for the barriers heights were taken from microwave spectroscopy and low-temperature heat-capacity measurements published in the literature [9-15]. Using this calibration curve and the cross-section slopes obtained for dimethyl-dichloro-silane, dimethyl-polysiloxane (silicone oil), and acetic anhydride, the average barrier heights for internal rotation of methyl groups have been estimated for these compounds and are presented in Table II.

TABLE II. ESTIMATED BARRIER HEIGHTS FOR INTERNAL ROTATION OF CH_3 GROUPS IN DIMETHYL-DICHLORO-SILANE, DIMETHYL-POLYSILOXANE (SILICONE OIL) AND ACETIC ANHYDRIDE

Compound	Wavelength range of least-squares fit (Å)	Scattering cross-section slopes ($b/\text{Å} \cdot H$)	Estimated barrier heights (kcal/mole)
$(CH_3)_2SiCl_2$	6.0 - 10.0	12.3 ± 0.5	~ 0
Dimethyl-polysiloxane	5.0 - 10.0	12.3 ± 0.3	~ 0
$(CH_3CO)_2O$	6.0 - 10.0	10.8 ± 0.3	~ 1

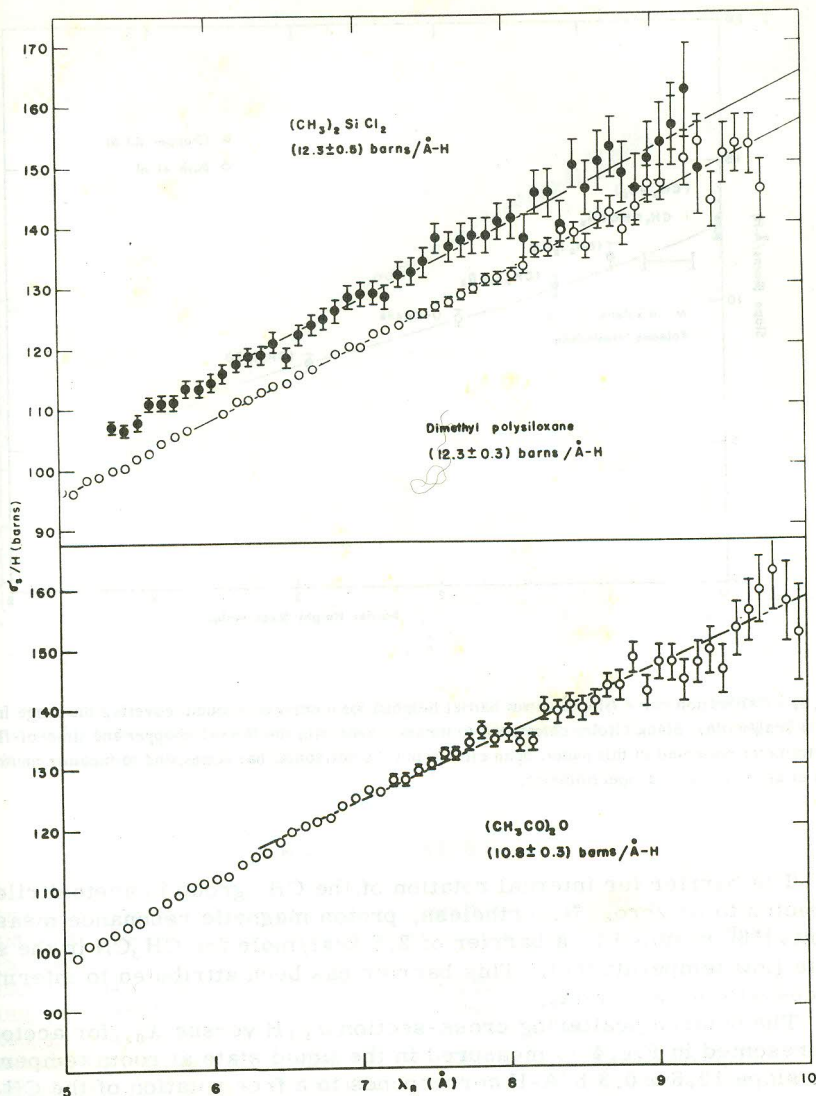


FIG. 2. Neutron-scattering cross-sections per hydrogen atom of dimethyl-dichloro-silane, dimethyl-polysiloxane (silicone oil) and acetic anhydride in the neutron wavelength range 5 to 10 Å. Slopes were calculated by a weighted least-squares fit to the data. Only statistical errors are indicated.

Dimethyl-dichloro-silane is used in the preparation of silicone polymers such as dimethyl-polysiloxane. The internal rotation of methyl groups in these compounds seems to be free, as had already been predicted [16-17].

The average barrier for internal rotation of the CH_3 groups in acetic anhydride has been estimated to be ~ 1 kcal/mole.

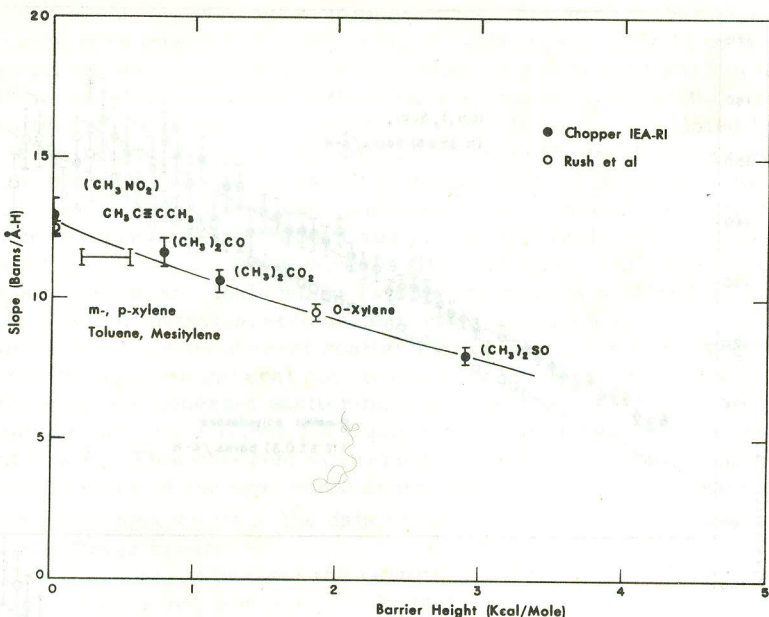


FIG. 3. Calibration curve (slopes versus barrier heights) for methyl compounds covering the range from 0 to 3 kcal/mole. Black circles correspond to measurement with the IEA-R1 chopper and time-of-flight spectrometer presented in this paper; open circles and the horizontal bar correspond to measurements by Rush et al, with a crystal spectrometer.

The barrier for internal rotation of the CH₃ group in acetonitrile is expected to be zero. Nevertheless, proton magnetic resonance measurements [18] resulted in a barrier of 2.6 kcal/mole for CH₃CN in the solid state (low temperatures). This barrier has been attributed to intermolecular forces within the crystal.

The neutron scattering cross-section σ_s/H versus λ_n , for acetonitrile, is presented in Fig. 4 as measured in the liquid state at room temperature. The slope 12.6 ± 0.3 b/Å-H corresponds to a free rotation of the CH₃ group, probably indicating that the influence of intermolecular forces is negligible for this compound in the liquid state.

As all substances in this paper can be considered as non-associated liquids, this last comment may be also extended to them.

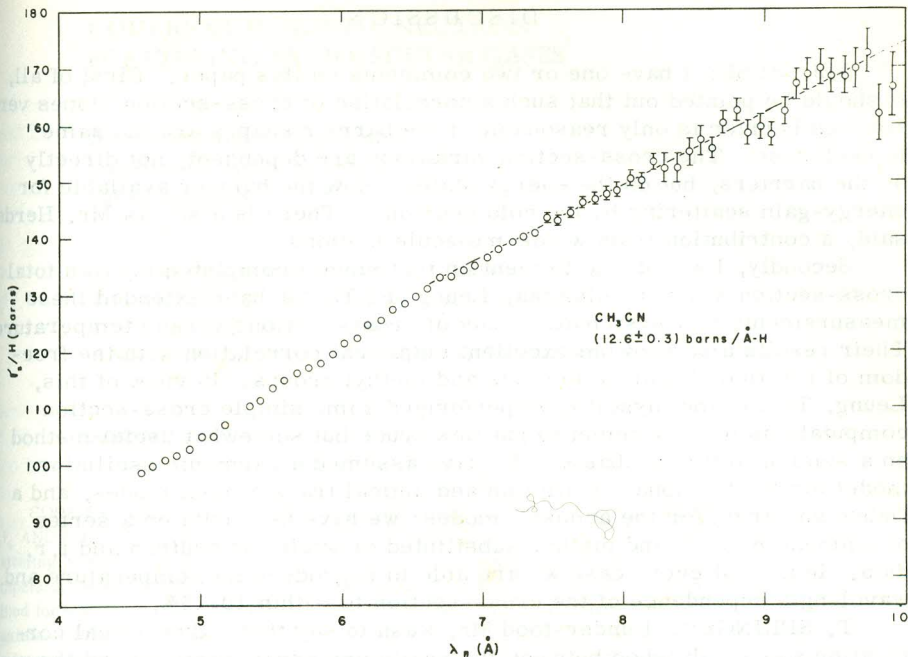


FIG. 4. Neutron-scattering cross-section per hydrogen atom of acetonitrile in the neutron wavelength range 4 to 10 Å. Cross-section slope for $\lambda_n > 6.5$ Å has been determined by a weighted least-squares fit to the data. Only statistical errors are indicated.

REFERENCES

- [1] RUSH, J. J., TAYLOR, T. I., *J. phys. Chem.* **68** (1964) 2534.
- [2] JANIK, J. M., *Inelastic Scattering of Neutrons* (Proc. Symp. Bombay, 1964) **2**, IAEA, Vienna (1965) 262.
- [3] RUSH, J. J., HAMILTON, W. C., *Inorg. Chem.* **5** (1966) 2238.
- [4] RUSH, J. J., LEUNG, P. S., TAYLOR, T. I., *J. chem. Phys.* **45** (1966) 1312.
- [5] RUSH, J. J., TAYLOR, T. I., HAVENS, W. W., *J. chem. Phys.* **37** (1962) 234.
- [6] HERDADE, S. B., AMARAL, L. Q., RODRIGUEZ, C., VINHAS, L. A., Rep. IEA-136 (1967).
- [7] AMARAL, L. Q., VINHAS, L. A., RODRIGUEZ, C., HERDADE, S. B., *Nucl. Instrum. Meth.* (to be published).
- [8] HUGHES, D. J., SCHWARTZ, R. B., *Neutron Cross Sections*, Rep. NBL-325 (1958) 2nd ed.
- [9] TANNENBAUM, G., MYERS, R. J. GWINN, W. D., *J. chem. Phys.* **25** (1956) 42.
- [10] LOWE, J. P., PARR, R. G., *J. chem. Phys.* **44** (1966) 3001, Table I.
- [11] WULF, C. A., *J. chem. Phys.* **39** (1963) 1227.
- [12] SIMPSON, K. O., BEYNON, E. T., *J. phys. Chem.* **71** (1967) 2796.
- [13] SWALEN, J. D., COSTAIN, C. C., *J. chem. Phys.* **31** (1959) 1562.
- [14] WILSON, E. B., "The problem of barriers to internal rotation in molecules", *Advances in Chemical Physics* **2**, Interscience Publishers, New York (1959).
- [15] DREIZLER, H., DENDL, G., *Z. Naturf. T1* **20** 11 (1965) 1431.
- [16] ROCHOW, E. G., "Silicones", *Modern Chemistry for the Engineer and Scientist* (ROBERTSON, G. R., Ed.), McGraw-Hill (1957).
- [17] ROCHOW, E. G., LE CLAIR, H. G., *J. inorg. nucl. Chem.* **1** (1955) 92.
- [18] STEJSKAL, E. O., WOESSNER, D. E., FARRAR, T. C., GUTOWSKY, H. S., *J. chem. Phys.* **31** (1959) 55.

DISCUSSION

J. J. RUSH: I have one or two comments on this paper. First of all, it should be pointed out that such a correlation of cross-section slopes versus rotation barrier is only reasonable if the barrier shapes are the same in each case. The cross-section variations are dependent, not directly on the barriers, but on the energy states below the barrier available for energy-gain scattering by the cold neutrons. There is also, as Mr. Herdade said, a contribution from whole-molecule motions.

Secondly, I would like to mention that since I completed my own total cross-section work at Columbia, Leung and Taylor have extended these measurements to a systematic study of cross-sections versus temperature. Their results also show an excellent empirical correlation with the freedom of rotation of ammonium ions and methyl groups. In view of this, Leung, Taylor and myself have performed some simple cross-section computations in an attempt to put this crude but somewhat useful method on a semi-quantitative basis. We have assumed a harmonic oscillator model for the torsional oscillation and optical translational modes, and a Debye spectrum for the acoustic modes; we have used data on a series of ammonium salts and methyl-substituted crystals for neutron and i. r. data. In almost every case we are able to reproduce the temperature and wavelength dependence of the cross-section to within 10-15%.

T. SPRINGER: I understood Mr. Rush to say that a theoretical correlation was established between the scattering cross-sections and the barrier heights: was this done assuming a cosine-shaped angular dependent potential for the hindered rotations, this potential directly connecting the torsional frequency with the barrier height?

J. J. RUSH: Perhaps I did not make myself quite clear. In our cross-section calculations we did not use rotational barriers; we assumed single frequencies for the torsional and translational modes and calculated cross-sections using the peak energies assigned from neutron and i. r. spectra. I don't believe that a more sophisticated approach is justified for fitting such integral data on relatively complex solids.