

## Nuclear Spin Resonance of Aqueous Sodium Ion

John E. Wertz and Oleg Jardetzky

Citation: *The Journal of Chemical Physics* **25**, 357 (1956); doi: 10.1063/1.1742886

View online: <http://dx.doi.org/10.1063/1.1742886>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/25/2?ver=pdfcov>

Published by the AIP Publishing

---

### Articles you may be interested in

Raman and nuclear magnetic resonance studies on the concentration dependence of orientational relaxation times of the nitrate ion in dilute aqueous solution

J. Chem. Phys. **90**, 392 (1989); 10.1063/1.456486

Nuclear relaxation and spinspin coupling in aqueous sodium molybdate

J. Chem. Phys. **61**, 4360 (1974); 10.1063/1.1681745

Nuclear Magnetic Resonance Study of the Protolysis of Trimethylammonium Ion in Aqueous Solution—Order of the Reaction with Respect to Solvent

J. Chem. Phys. **39**, 366 (1963); 10.1063/1.1734254

Proton Transfer Studies by Nuclear Magnetic Resonance. I. Diffusion Control in the Reaction of Ammonium Ion in Aqueous Acid

J. Chem. Phys. **33**, 547 (1960); 10.1063/1.1731182

Electron Spin Resonance of Colloidal Sodium in Sodium Azide

J. Chem. Phys. **32**, 940 (1960); 10.1063/1.1730822

---



## Letters to the Editor

**T**HIS section will accept reports of new work, provided these are terse and contain few figures, and especially few half-tone cuts. The Editorial Board will not hold itself responsible for opinions expressed by the correspondents. Contributions to this section should not exceed 600 words in length and must reach the office of the Editor not later than the 15th of the second month preceding that of the issue in which the Letter is to appear. No proof will be sent to the authors. The publication charge for Letters is \$25 per page, with a minimum of \$25 per Letter. If honored, the Institution will be entitled to 100 reprints without covers.

### Temperature Dependence of the Heat Capacity of Gases

HUGH M. SPENCER

Cobb Chemical Laboratory, University of Virginia, Charlottesville, Virginia  
(Received June 1, 1956)

**B**ERNSTEIN<sup>1</sup> stated that "the temperature dependence of the heat capacity (of an ideal gas) is given as a quadratic in  $1/T$  rather than  $T$  as is most often encountered in the literature." In partial justification of this statement he compared the success with which equations of these forms fitted to  $C_p^0$  for gaseous  $\text{CCl}_4$ , 300 to 1000°K, reproduce the data.

The temperature-dependent parts of the heat capacities of ideal gases are compounded of the contributions of the fundamental frequencies (s- and reverse s-shaped *vs*  $T$  and  $1/T$ ), and in smaller amounts, in the case of some substances, of one or more hindered rotations<sup>3</sup> (reverse s- and s-shaped *vs*  $T$  and  $1/T$ ). Thus  $C_p^0$  plotted *vs*  $T$  or  $1/T$  resembles the familiar representations of the Einstein function of a single frequency. No one three-constant power series in a  $T$  equation will most satisfactorily represent the heat capacity over the ranges of temperature for the various substances in which we are interested. In addition to equations of the form

$$C_p^0 = a + bT + cT^2 \quad (1)$$

several other simply manipulated empirical equations of the forms

$$C_p^0 = a' + b'T + c'/T^2 \quad (2)^4$$

$$C_p^0 = a'' + b''/T + c''/T^2 \quad (3)^5$$

$$C_p^0 = a''' + b'''/T^{\frac{1}{2}} + c'''/T \quad (4)^5$$

$$C_p^0 = a'''' + b''''/T^{\frac{1}{2}} + c''''/T \quad (5)^6$$

have been found to represent the temperature dependence of the heat capacity with satisfactory accuracy in certain cases.

If the variable part of the heat capacity results principally from contributions of high frequencies, i.e., high  $\omega_i/T$ 's, equations of type 1 are the most satisfactory, and if the contributions of low  $\omega_i/T$ 's are most important and the range of temperature is relatively great, equations involving the reciprocal powers have been most useful. For curves of the first kind the change of curva-

ture with respect to the  $T$  axis is greater at the higher temperatures of the range, and vice versa. In Table I are comparisons of equations of types (1) and (3) for several gases in the first category and for one ( $n\text{-C}_6\text{H}_{14}$ ) which is a borderline case. For these gases, equations of type (1) are also superior to equations of type (2). It has been recognized<sup>7-9</sup> that equations of type (1) are unsatisfactory for many gases over interesting ranges of temperature. Equations of type (2) for 23 substances, including  $\text{CCl}_4$  (Vold's data, 0 to 500°C) have been published. (For  $\text{Br}_2$ ,  $c' \times 10^6$  should read  $-0.298$ .) In note 22 of reference 7 the superiority of Sweigert and Beardsley's<sup>5</sup> equation of type (3) to equations of types (1) and (2) was pointed out. However, for  $\text{CCl}_4$  the equation

$$C_p^0 = 23.908 + 1.613 \times 10^{-3}T - (3.989 \times 10^5)/T^2, \quad (6)$$

fitted (1952) to the whole range of data, 298.16 to 1000°K,<sup>2</sup> reproduces the data as well as Bernstein's equation of type (3).

It has been the writer's feeling that if three constant equations of types (1) and (2), which are also the types most frequently encountered in the representation of solids (and liquids), do not represent the data accurately enough that the use of the quite generally adequate four constant ( $T^3$ ) equations is preferable to the use of equations of types (3), (4), and (5). Equations of type (3) seem to be more versatile than those of type (2) in the representation of  $C_p^0$ 's of gases. If it also turned out that the heat capacities of solids at high temperatures were satisfactorily represented by equations of type (3) and were generally available in that form it would seem wise to report the data for gases in equations of types (1) and (3), and the  $T^3$  equation where necessary.

<sup>1</sup> H. J. Bernstein, J. Chem. Phys. **24**, 911 (1956).

<sup>2</sup> J. R. Madigan and F. F. Cleveland, J. Chem. Phys. **19**, 119 (1951).

<sup>3</sup> K. S. Pitzer and W. D. Gwinn, J. Chem. Phys. **10**, 428 (1942), or see W. B. Person and G. C. Pimentel, J. Am. Chem. Soc. **75**, 532 (1953).

<sup>4</sup> K. K. Kelley, U. S. Bureau of Mines Bull. No. 371 (1934).

<sup>5</sup> R. L. Sweigert and W. M. Beardsley, Georgia School of Tech. State Eng. Expt. Sta. Bull. No. 2 (1938).

<sup>6</sup> J. Chipman and M. G. Fontana, J. Am. Chem. Soc. **57**, 48 (1935).

<sup>7</sup> H. M. Spencer and G. N. Flannagan, J. Am. Chem. Soc. **64**, 2511 (1946).

<sup>8</sup> H. M. Spencer, Ind. Eng. Chem. **40**, 2152 (1948).

<sup>9</sup> H. M. Spencer, J. Am. Chem. Soc. **67**, 1859 (1945).

### Nuclear Spin Resonance of Aqueous Sodium Ion\*

JOHN E. WERTZ AND OLEG JARDETSKY†

Departments of Chemistry and Physiology, University of Minnesota,  
Minneapolis, Minnesota

(Received June 14, 1956)

**N**UCLEAR spin resonance absorption of ionic sodium in aqueous solutions of inorganic salts has been studied in a field of 7030 gauss. Although the absorption line is observable directly on an oscilloscope, it was found convenient to record its derivative. The shape of the derivative was found to correspond very closely to that of a Gaussian curve. The line width between points of maximum slope for the 3-M NaCl standard was found to be about 32 mgauss. Although this width is much greater than that for proton lines, it is much less than the 0.2-gauss width for  $\text{Cl}^{35}$  as the chloride ion,<sup>1</sup> although  $\text{Na}^{23}$  and  $\text{Cl}^{35}$  have quadrupole moments of similar magnitude.

Line widths and amplitudes were measured on a number of solutions of inorganic sodium salts at varying concentrations. Within the error of measurement no shifts have been detected. On the other hand, definite differences in line widths and amplitudes have been found. When plotted as functions of concentration the curves follow one of two distinct patterns.

(1) In the first case the width remains constant from concentrations of about 0.1 M to the limit of solubility, and the amplitude increases linearly with concentration. Typical of this behavior are NaCl, NaF, NaBr,  $\text{Na}_2\text{S}$ ,  $\text{NaN}_3$ ,  $\text{Na}_2\text{SO}_4$ . Of special interest is  $\text{Na}_3\text{Fe}(\text{CN})_6$ , which also falls into this category, although it has a paramagnetic anion. In similar experiments on  $\text{Cl}^-$  in aqueous salt solutions, paramagnetic cations usually have a profound effect on the width, intensity, and resonant field values,<sup>1</sup>

TABLE I. Comparison of equations of types (1) and (3).<sup>a</sup>

Gas	$a''$	$b'' \times 10^{-3}$	$c'' \times 10^{-5}$	% Deviation Eq. (3)		% Deviation Eq. (1)		Source of Eq. (1)
				Aver- age	Maxi- mum	Aver- age	Maxi- mum	
$\text{H}_2$	8.1365	-1.0104	1.9463	1.09	2.13	0.19	0.49	(7)
$\text{H}_2\text{O}$	13.3430	-4.0323	7.3763	1.56	3.75	0.40	0.96	(8)
$\text{CH}_4$	27.9189	-12.5764	20.3899	1.44	5.28	0.52	1.80	(9)
$\text{C}_2\text{H}_6$	46.6501	-20.0861	29.7654	1.10	4.01	0.42	0.75	(9)
$n\text{-C}_6\text{H}_{14}$	120.046	-47.2752	65.7298	0.75	2.50	0.87	1.88	(9)
$\text{cis-2-C}_6\text{H}_{14}$	105.548	-40.0721	52.7594	0.47	1.19	0.25	0.47	(9)

<sup>a</sup> For  $\text{cis-2-hexene}$  the temperature range is 298.16–1000°K, for the other gases 298.16–1500°K.

(2) In the second category are compounds for which line width increases with concentration, while the amplitude levels off or actually goes through a maximum. This behavior usually becomes evident at relatively high concentrations, generally above 6*N*. NaOH shows a maximum of about 7–8*N* and a rapid decline of line intensity at higher concentrations. Because of its high solubility, it permits the observation of very broad and weak lines on 18*N* solutions. NaClO<sub>4</sub>, NaI, and NaSCN also follow the same pattern. In all of these cases the line width at lower concentration (up to 3–4*N*) is the same as that of the standard, with comparable amplitudes. On the other hand, solutions of Na<sub>3</sub>PO<sub>4</sub> and Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> show broader lines at considerably lower concentrations (1–2*N*) and the amplitude reaches a maximum (Na<sub>3</sub>PO<sub>4</sub>) or a plateau (Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>) before the limit of solubility is reached. The reduction in signal amplitudes is usually far greater than that expected from the line width.

The observed broadening and decrease in line amplitude is likely due to quadrupolar interactions, reflecting departures from effectively spherical symmetry of charge distribution around the sodium nucleus, such as would occur in ion pair or complex formation. We assume that appreciable quadrupole interaction broadens the line beyond detection, and hence that we observe resonance only for almost purely ionic sodium. Marked tendency toward ion pair formation should occur when the water available is insufficient for complete hydration of the Na<sup>+</sup> ions. In some of the more viscous solutions such as concentrated NaOH some broadening could perhaps be expected from a shortening of the thermal relaxation time.

The experimental material is being extended. Data on the interaction of sodium with organic compounds are to be published elsewhere.

The authors express their thanks to Dr. W. N. Lipscomb, for suggesting the study of active transport of sodium by this approach. Thanks are also due Frisic Dravnieks and T. Hines for considerable technical assistance.

\* This research was supported by the U. S. Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF18(603)–17.

† Research fellow of the American Heart Association.

‡ John E. Wertz, *J. Chem. Phys.* **24**, 484 (1956).

## Effect of Gases on the Photoconductivity of Anthracene

W. G. SCHNEIDER AND T. C. WADDINGTON\*

Division of Pure Chemistry, National Research Council, Ottawa, Canada

(Received June 13, 1956)

**F**OLLOWING the observations of Vartanyan,<sup>1</sup> of Chynoweth<sup>2</sup> and of Bree, Carswell, and Lyons<sup>3</sup> that the surface photoconductivity of an anthracene crystal is increased by the presence of oxygen gas, we have examined the effects of a number of gases and vapors on the photoconductivity of anthracene in the surface cell.

The behavior of these gases falls into four classes: (1) Cl<sub>2</sub> and NO<sub>2</sub> produce a permanent increase in the photo- and semiconductivity; the spectral dependence of the photoconductivity is altered, the crystal changes color, and the anthracene fluorescence is suppressed. These changes are probably due to chemical reaction<sup>4,5</sup> and will be discussed further elsewhere.

(2) BF<sub>3</sub>, HCl, SO<sub>2</sub>, NO, and O<sub>2</sub> all produce a marked increase in the photocurrent in anthracene and appear to increase the dark current also. All these gases appear to be strongly adsorbed and the return of the photocurrent to its original high vacuum value takes place only after several hours pumping even while the crystal is illuminated; a much longer time is necessary in the dark.

(3) NH<sub>3</sub>, (CH<sub>3</sub>)<sub>3</sub>N, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, H<sub>2</sub>O and (CH<sub>3</sub>)<sub>2</sub>CO all decrease the photocurrent markedly. In general on pumping the photocurrent returns to its high vacuum value much more

rapidly than after exposure to the gases in class (2), although both NH<sub>3</sub> and (CH<sub>3</sub>)<sub>3</sub>N are fairly strongly adsorbed and require some time to pump off.

(4) CO<sub>2</sub>, N<sub>2</sub>, A, and (CH<sub>3</sub>)<sub>4</sub>C have no effect on the photoconductivity of anthracene.

It will be seen that all the gases in classes (1) and (2) are of the type described by molecular complex theory as electron acceptors while those of class (3) are all electron donors and possess lone pair electrons. The gases in class (4) are of the type described as inert although CO<sub>2</sub> can act both as a very weak donor and acceptor. It seems unlikely that the behavior of all these gases can be due to any definite compound formation as was postulated by Lyons *et al.*<sup>3</sup> to explain the behavior of oxygen.

The effect of the gases on the photocurrent almost certainly arises in one of two ways: (a) an effect on the formation of charge carriers; this, Lyons has suggested,<sup>6</sup> takes place at the surface or (b) a change in the surface mobility of the carriers. These gases are found to have comparatively small effects on the photoconductivity of a sandwich cell as compared to their very large effects on the surface cell. This indicates that (b) is probably the correct alternative. Preliminary experiments on sandwich cells in which the surface current is totally eliminated by the use of a guard ring bear this out.

The explanation of this behavior is probably the effect the various gases have on the surface dipole or electric double layer, which in turn modifies the surface energy levels and traps, as was pointed out for the case of germanium by Brattain and Bardeen.<sup>7</sup> The gases in class (2) tend to accept electrons and thereby decrease the positive hole trapping whereas the gases in class (3) tend to donate electrons and thereby increase the positive hole trapping. If positive holes are the majority carriers, as suggested by Chynoweth and Schneider<sup>8</sup> and by Goldsmith,<sup>9</sup> then the behavior of the surface photocurrent is explained. The observations of Picke and Wissman<sup>10</sup> on the effect of O<sub>2</sub> on the semiconductivity of naphthalene and of Liebson<sup>11</sup> on the effect of NH<sub>3</sub> and O<sub>2</sub> on the photoconductivity of CdS suggest strongly that the gas effect may occur in any photoconductor or semiconductor in which surface currents play an important part.

\* N. R. L. Post-doctorate Fellow.

<sup>1</sup> Vartanyan, *Doklady. Akad. Nauk. S.S.S.R.*, **71**, 641 (1950).

<sup>2</sup> Chynoweth, *J. Chem. Phys.*, **22**, 1029 (1954).

<sup>3</sup> Bree, Carswell, and Lyons, *J. Chem. Soc.* 1728 (1955).

<sup>4</sup> Lieberman, *Ber. deut. chem. Ges.*, **13**, 1584 (1880).

<sup>5</sup> Meisenheimer and Connerade, *Ann. Chem.*, **330**, 133 (1904).

<sup>6</sup> Lyons, *J. Chem. Phys.*, **23**, 220 (1955).

<sup>7</sup> Brattain and Bardeen, *Bell System Tech. J.*, **32**, 1 (1953).

<sup>8</sup> Chynoweth and Schneider, *J. Chem. Phys.*, **22**, 1021 (1954).

<sup>9</sup> Goldsmith, Ph.D. thesis, Purdue (1955).

<sup>10</sup> Picke and Wissman, *Z. Physik*, **138**, 436 (1954).

<sup>11</sup> Liebson, *J. Chem. Phys.*, **23**, 1732 (1955).

## Internal Barrier in CH<sub>3</sub>CH<sub>2</sub>F and CH<sub>3</sub>CHF<sub>2</sub> from Torsional Satellites\*

DUDLEY R. HERSCHBACH†

Department of Chemistry, Harvard University, Cambridge 38, Massachusetts

(Received June 11, 1956)

**T**HE barriers to internal rotation of a methyl group in several molecules have recently been accurately determined by exploiting the tunnel effect,<sup>1</sup> which splits each torsional state *v* into a nondegenerate level, *V<sub>A</sub>*, and a doubly-degenerate level, *v<sub>B</sub>*. Since molecules in these two levels have slightly different rotational transition frequencies, doublets with barrier dependent separation are observed in the microwave spectrum. However, the applicability of this method has been limited to molecules with barriers less than 1800 cal, typically, because the splittings rapidly decrease as the barrier increases.

In order to obtain an observable magnification for CH<sub>3</sub>CH<sub>2</sub>F and CH<sub>3</sub>CHF<sub>2</sub>, we have studied the rotational spectrum of molecules in the first excited torsional state in which the tunneling (and, roughly, the doublet splitting) is about 70 times greater.