Variation of chemical shielding with intermolecular interaction and rovibrational motion. V. ^{15}N in N_2

Cynthia J. Jameson

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

A. Keith Jameson

Department of Chemistry, Loyola University, Chicago, Illinois 60626

S. Wille and Patricia M. Burrell

Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680

(Received 8 September 1980; accepted 30 September 1980)

The ^{15}N resonance frequency in $^{15}N_2$ gas has been measured as a function of density and temperature. The effect of intermolecular interactions, which is observed as a density dependence, is about the same magnitude as that for ^{13}C in two interacting CO molecules, but smaller than previously observed for ^{15}N nuclei in other molecules. The temperature dependence in the zero-pressure limit $[\sigma_0(T) - \sigma_0(300) = -(0.85 \pm 0.10) \times 10^{-3} (T - 300)$ ppm] originates from centrifugal distortion. The effect of vibrational averaging contributes negligibly to the temperature dependence in the range 220–380 K. Comparison with previous theoretical calculations of ^{15}N shielding in N_2 as a function of internuclear separation shows reasonably good agreement with the observed temperature dependence in the zero-pressure limit. The results for the N_2 system are compared with the isoelectronic CO molecule for which more precise ^{13}C NMR measurements are also reported here.

INTRODUCTION

The nuclear magnetic shielding of a nucleus in a molecule is affected by intermolecular interactions and intramolecular motion. In the gas phase, these effects are observed as a dependence of the nuclear resonance frequency on density and temperature. When gases of moderate densities are studied, it has been found that, at a given temperature, there is a linear dependence of the nuclear resonance frequency on density.[1] Under these conditions, only the terms in $\sigma_0(T)$ and $\sigma_1(T)$ need be considered in the virial expansion of the nuclear magnetic shielding in terms of density ρ:

$$\sigma(T,\rho) = \sigma_0(T) + \sigma_1(T)\,\rho + \sigma_2(T)\,\rho^2 + \cdots \quad . \tag{1}$$

Intermolecular interactions are temperature dependent, so we expect to get a temperature dependent second virial coefficient of nuclear shielding $\sigma_1(T)$.[2] In the limit of very low pressure, the intermolecular effects on σ are no longer important; however, there will still be enough collisions such that an average over rovibrational states is observed. Thus, the temperature dependent nuclear magnetic shielding which is observed in the limit of zero pressure is effectively that for an "isolated" molecule with rotationally and vibrationally averaged nuclear shielding $\sigma_0(T)$. We have reported $\sigma_0(T)$ and $\sigma_1(T)$ for several systems.[3–9]

The simplest system to study, insofar as the interpretation of $\sigma_1(T)$ is concerned, is a rare gas. The intermolecular potential between two rare gas atoms is a spherically symmetric one and $\sigma_1(T)$ has a simple form:

$$\sigma_1(T) = 4\pi \int_0^\infty \sigma(R) \exp[-V(R)/kT] R^2\, dR \,. \tag{2}$$

For these studies the ^{129}Xe nucleus was an ideal probe.[2] On the other hand, insofar as the interpretation of $\sigma_0(T)$ is concerned, the simplest system to study is a diatomic molecule. The temperature and density dependence of nuclear shielding has been measured in some diatomic molecules: ^1H in HCl[1] and HBr (Ref. 10), ^{13}C in CO (Refs. 11 and 12), ^1H and ^{19}F in HF (Ref. 13), ^{19}F in ClF and F_2.[12] The advantages are as follows: In a diatomic molecule there is only one internal coordinate, i.e., $\Delta r = (R - R_e)$, or the dimensionless coordinate $\xi = (R - R_e)/R_e$. Thus, the shielding in the isolated diatomic molecule is a function of only one coordinate. There exist theoretical calculations of nuclear magnetic shielding in many diatomic molecules for configurations other than the equilibrium nuclear configuration, so that derivatives $(d\sigma/d\xi)_e$ and $(d^2\sigma/d\xi^2)_e$ are available.[14] In addition, molecular beam resonance experiments have been carried out on diatomic molecules, and an experimental value for the paramagnetic part of the shielding is obtained from the relationship with the spin–rotation constant.[15] When used with a reliable theoretical value for the diamagnetic part, these provide an absolute measure of σ. The theoretical values for the diamagnetic part are considered to be very reliable.[16] Extensive configuration interaction calculations give results which are essentially identical to those obtained from a single configuration SCF calculation. Thus, good estimates of absolute shielding exist for many diatomic molecules. In addition, the anharmonic force field of diatomic molecules are well known, as opposed to polyatomic molecules; due to the single internal coordinate in which the force field is expressed.

The N_2 molecule is of special interest because calculations of σ as a function of internuclear separation and molecular beam studies exist.[17,18] N_2 is one of the key molecules in the ^{15}N or ^{14}N nuclear shielding scale which has yet to be established. Some problems of internal consistency between molecular beam results on individ-

J. Chem. Phys. 74(2), 15 Jan. 1981 0021-9606/81/020853-04$01.00

ual molecules containing N and the reported N chemical shifts between them have been pointed out.[19] In addition, comparison of σ_1 and σ_0 of ^{15}N in N_2 with the isoelectronic CO is useful. CO has been the subject of similar calculations of σ as a function of internuclear separation and molecular beam resonance studies,[20,21] as well as density and temperature dependent measurements of ^{13}C resonance in the gas phase.[11,12] We have previously reported the σ_1 and $\sigma_0(T)$ of ^{13}C in CO.[12] In this paper, we discuss the results of the variation of the ^{15}N chemical shift with temperature and density in $^{15}N_2$ gas. We have also repeated ^{13}C in CO measurements in order to be able to compare the ^{15}N results with more precise ^{13}CO data.

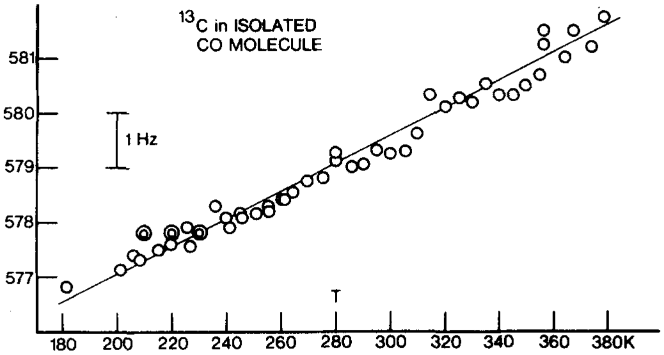

FIG. 2. The temperature dependence of ^{13}C. shielding in an isolated molecule of CO, remeasured at 22.633 MHz with improved precision over Ref. 12. Unlike Fig. 1, this plot includes the temperature dependence of the lock substance.

EXPERIMENTAL RESULTS

Nitrogen nuclear resonance has been previously observed in N_2. ^{14}N in liquid N_2 was reported to be either 14 or 70 ppm upfield of NO_3^- ion.[22,23] The linewidths limited the accuracy of the results. Recently, ^{15}N resonance in liquid N_2 (natural abundance) at 77 K was observed 65.6 ppm upfield from the $^{15}NO_3^-$ resonance in a 5 M solution of $^{15}NH_4^+$ $^{15}NO_3^-$ in 2 M nitric acid at 300 K.[24] More recently, ^{15}N in N_2 gas was observed 75.3 ppm upfield of liquid CD_3NO_2 containing $Cr(acac)_3$.[25] No temperture or density dependence of the nitrogen resonance in N_2 has been reported for either gas or liquid.

$^{15}N_2$ (99 at. %) was used directly as obtained from Stohler Isotopes. N_2 has a substantial vapor pressure when transfers are made under liquid nitrogen, so corrections for remaining gas in the very small (less than 1 ml) dead volume were necessary. With this correction we estimate our measured densities to have no more than 2% relative error. The ^{15}N FT NMR spectra were taken on a Bruker spectrometer operating at 21.1 kG, using a ^2D lock (the CD_3 in toluene-*d*8) to stabilize the field. Temperature regulation and other experimental details have been described previously.[26,27] Spectra of samples with densities ranging from 20 to 145 amagat were taken from 220 to 360 K. Repetition rates of 5 to 30 s were used, accumulating between 200 and 4096 FID's in 2 to 4 K of memory, zero filling to 8 K. Linewidths were typically 2 to 10 Hz at 9.122 MHz depending on the density and temperature. Plots of ^{15}N resonance frequencies with temperature for each sample of a given density were found to be linear, and for samples of various densities were found to be parallel within experimental error. Thus, we report a constant $\sigma_1 = -(4.26 \pm 0.13) \times 10^{-3}$ ppm/amagat. When the density dependent contribution is removed as $\sigma_1 \rho$ and the absolute temperature dependence of the CD_3 signal of toluene-*d*8 is subtracted from the raw data, we obtain the resonance frequencies in the zero pressure limit, the "isolated" molecule resonance frequencies. These are shown in Fig. 1. The behavior appears to be linear, unlike ^{19}F in ClF and F_2.[12] From the slope of the straight line fitted to these data points we get for ^{15}N in N_2, $\sigma_0(T) - \sigma_0(300) = -(0.85 \pm 0.10) \times 10^{-3} (T-300)$ ppm. The error quoted here includes only the scatter in the ^{15}N data. There is an additional uncertainty of $\pm 0.12 \times 10^{-3}$ppm/deg due to the errors intrinsic in the absolute temperature dependence of the reference.[28]

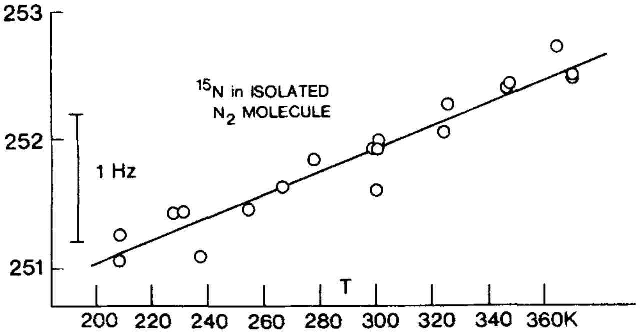

FIG. 1. The temperature dependence of ^{15}N shielding in an isolated molecule of N_2, obtained by reducing resonance frequencies measured at 9.122 MHz in samples of various densities to the zero-density limit.

Our earlier ^{13}C in CO results were less precise than the present ^{15}N data. In order to compare our ^{15}N in N_2 results with the ^{13}C in ^{13}CO in a meaningful way, we repeated the ^{13}C temperature and density dependent measurements. The results are shown in Fig. 2 from which we obtain, for ^{13}C in CO, $\sigma_0(T) - \sigma_0(300) = -(2.906 \pm 0.4) \times 10^{-4} (T-300)$ ppm, which agrees with the previous results within the quoted errors.[12]

DISCUSSION

The second virial coefficient (σ_1) for ^{15}N in N_2 is essentially the same as that for ^{13}C in CO, not surprising at all since they are isoelectronic and have very similar intermolecular potential parameters.[29] The value of σ_1 for ^{15}N in N_2 can be compared with the other ^{15}N values which have previously been measured: -0.0099 ppm/amagat for ^{15}N(end) in NNO, -0.0030 for ^{15}N(center) in NNO,[4] and -0.41 for ^{15}N in NH_3.[30] Only about 25% of σ_1 is due to the bulk susceptibility contribution which, coincidentally, is the same (-0.0011 ppm/amagat) as that for CO.[31] Most of σ_1 is due to pairwise interaction between two N_2 molecules.

The interpretation of the temperature dependence of $\sigma_0(T)$ for a diatomic molecule has been previously con-

TABLE I. Comparison of experimental and theoretical results for nitrogen shielding in N_2 and carbon shielding in CO all in ppm.

	^{15}N in N_2		^{13}C in CO	
	Theor.	Expt.	Theor.	Expt.
σ_e	-19.79^a		$+11.48^b$	
$\langle\sigma\rangle^{0\,K}$	-23.18^a		$+9.35^c$	
$\langle\sigma\rangle \simeq \sigma^p + \sigma_e^d$ (theor.)		-101 ± 20^d		$+5.0^{e,c}$ $+3.20 \pm 0.27^h$
$(d\sigma/d\xi)_e$	-700.6^a	-850 ± 100^f	-466.5^b	-255 ± 50^f
$(\langle\sigma\rangle^T - \langle\sigma\rangle^{300})/(T-300)$	$-7.0\times 10^{-4\,g}$	$-(8.5 \pm 1.0)\times 10^{-4\,f}$	$-5.3\times 10^{-4\,g}$	$-(2.906 \pm 0.4)\times 10^{-4\,f}$
$\langle\sigma\rangle^{300} - \langle\sigma\rangle^{0\,K}$	-0.210^g	-0.255^f	-0.159^g	-0.087^f

[a] Reference 17.
[b] Reference 20.
[c] W. T. Raynes and G. Stanney, J. Magn. Reson. **14**, 378 (1974).
[d] Reference 18.
[e] Reference 21.
[f] This work.
[g] Calculated using theoretical $(d\sigma/d\xi)_e$ in Eq. (13).
[h] D. B. Neumann and J. W. Moskowitz, J. Chem. Phys. **50**, 2216 (1969).

sidered.[32,33] The expansion of σ for a nucleus in an isolated molecule in terms of the dimensionless coordinate $\xi = (R - R_e)/R_e$ is[32]

$$\sigma(\xi) = \sigma_e + (d\sigma/d\xi)_e\, \xi + \tfrac{1}{2}(d^2\sigma/d\xi^2)_e\, \xi^2 + \cdots \quad . \qquad (3)$$

By treating the anharmonicity and the centrifugal distortion as perturbations to the harmonic oscillator, ξ and ξ^2 can be evaluated for a given rovibrational state as

$$\xi_{v,J} = -3a_1(B_e/\omega_e)(v + \tfrac{1}{2}) + 4(J^2 + J)(B_e/\omega_e)^2 \ , \qquad (4)$$

$$\xi^2_{v,J} = 2(B_e/\omega_e)(v + \tfrac{1}{2}) \ , \qquad (5)$$

where a_1 is the cubic anharmonic constant which is related to the other molecular constants as

$$a_1 = -[1 + (\alpha\omega_e/6B_e^2)] \ , \qquad (6)$$

in which ω_e is the harmonic frequency of vibration, and B_e and α are the rotational and the vibrational-rotational interaction constants, respectively. Thus, the shielding characteristic of a particular v, J state is given by

$$\sigma_{v,J} = \sigma_e + (v + \tfrac{1}{2})(B_e/\omega_e)[(d^2\sigma/d\xi^2)_e - 3a_1(d\sigma/d\xi)_e] + 4(J^2 + J)(B_e/\omega_e)^2(d\sigma/d\xi)_e + \cdots \quad . \qquad (7)$$

The observed nuclear shielding is a statistical average. At temperature T,

$$\langle v + \tfrac{1}{2}\rangle = \tfrac{1}{2}\coth(hc\omega_e/2kT) \ , \qquad (8)$$

$$\langle J^2 + J\rangle = kT/hcB_e \ , \qquad (9)$$

in which the proper average over discrete quantum states are carried out for vibration and a classical average for rotation. Using these, the thermal average of σ is

$$\langle\sigma\rangle^T = \sigma_e + (B_e/2\omega_e)[(d^2\sigma/d\xi^2)_e - 3a_1(d\sigma/d\xi)_e] \times \coth(hc\omega_e/2kT) + (4kT/hc)(B_e/\omega_e^2)(d\sigma/d\xi)_e + \cdots \qquad (10)$$

and

$$\langle\sigma\rangle^{0\,K} = \sigma_e + (B_e/2\omega_e)[(d^2\sigma/d\xi^2)_e - 3a_1(d\sigma/d\xi)_e] \ . \qquad (11)$$

In actual practice, what is observed is the difference between the average shielding at any temperature and some chosen standard temperature such as 300 K:

$$\langle\sigma\rangle^T - \langle\sigma\rangle^{300} = (B_e/2\omega_e)[(d^2\sigma/d\xi^2)_e - 3a_1(d\sigma/d\xi)_e] \times [\coth(hc\omega_e/2kT) - \coth(hc\omega_e/2k300)] + (4k/hc)(B_e/\omega_e^2)(d\sigma/d\xi)_e(T - 300) \ . \qquad (12)$$

For molecules with high harmonic frequencies, such as CO and N_2, $\coth(hc\omega_e/2kT)$ is essentially unity at low temperatures and remains virtually unchanged over the range of temperatures covered here (up to 380 K). Thus, for these molecules, the vibrational contribution to the shielding remains constant and the temperature dependence observed is nearly entirely due to the centrifugal distortion:

$$\langle\sigma\rangle^T - \langle\sigma\rangle^{300} \simeq (4k/hc)(B_e/\omega_e^2)(d\sigma/d\xi)_e(T - 300) \ . \qquad (13)$$

Experimentally, we should observe a linear plot of $\langle\sigma\rangle^T - \langle\sigma\rangle^{300}$, the resonance shift with temperature at the zero pressure limit (Fig. 1). The above function is independent of the isotopic composition of the CO or N_2 molecule. Although B_e and ω_e are both mass dependent, the ratio (B_e/ω_e^2) is not. The derivative $(d\sigma/d\xi)_e$ is also mass independent.

From our experimental results, we have $(4k/hc)(B_e/\omega_e^2)(d\sigma/d\xi)_e = -(0.85 \pm 0.10)\times 10^{-3}$ ppm/deg for ^{15}N in N_2 and $-(0.291 \pm 0.04)\times 10^{-3}$ ppm/deg for ^{13}C in CO. Thus, we have an empirical measurement of $(d\sigma/d\xi)_e$. There exist theoretical values of $(d\sigma/d\xi)_e$ for both molecules from the work of Stevens *et al.*[17,20] A comparison of the theoretical and empirical results are shown in Table I. The theoretical values are from coupled Hartree–Fock calculations of the second-order magnetic properties of N_2 by Laws, Stevens, and Lipscomb[17] and of CO by Stevens and Karplus.[20] The experimental values from

Ramsey *et al.*[18,21] correspond to essentially the ground vibrational state. Thus, the numbers in the second and third lines of Table I should be directly comparable. The ^{15}N in N_2 is indeed calculated to be antishielded relative to the bare nucleus, but the magnitude is too small compared with experiment. The "experimental" value is actually a composite of the experimental paramagnetic part of σ and a theoretical diagmagnetic part of σ. The latter is considered to be very reliable (error less than a few tenths of a ppm) so that for practical purposes the composite can be considered an experimental value. Our experimental results are compared in line 5 of the table with those calculated with Eq. (13) using (B_e/ω_e^2) from spectroscopy[34,35] and $(d\sigma/d\xi)_e$ from Stevens *et al.*[17,20] We see that they are in good agreement. A large part of this derivative is due to the variation of the paramagnetic contribution to σ with internuclear separation. The paramagnetic contribution is somewhat underestimated by theory, but the calculated derivative appears to be quite good. Using Eq. (13) we can obtain an empirical $(d\sigma/d\xi)_e$ also. These are compared to the theoretical values in the fourth line of Table I. The magnitude of the rovibrational correction is seen in the second and last lines. The vibrational correction is given by $\langle\sigma\rangle^{0\text{ K}} - \sigma_e$, about 2 to 3 ppm for N_2 and CO. The rotational correction is given by $\langle\sigma\rangle^{300} - \langle\sigma\rangle^{0\text{ K}}$, since the vibrational contribution is essentially constant over this temperature range for a diatomic molecule with a very high vibrational frequency. In other molecules (such as ClF and F_2) the rotational contribution to the temperature dependence is smaller than that from vibration.[33] The very small temperature dependence of σ_0 observed in N_2 and CO, compared to F_2[12] for example, is due to the lack of a vibrational contribution. The latter becomes comparable to the rotational contribution in N_2 and CO above 1000 K.

ACKNOWLEDGMENT

This research has been supported in part by National Science Foundation grants to The University of Illinois at Chicago Circle (CHE77-09133) and Loyola University (CHE77-09197).

[1] W. T. Raynes, A. D. Buckingham, and H. J. Bernstein, J. Chem. Phys. **36**, 3481 (1962).

[2] A. K. Jameson, C. J. Jameson, and H. S. Gutowsky, J. Chem. Phys. **53**, 2310 (1970).

[3] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **67**, 2771 (1977).

[4] C. J. Jameson, A. K. Jameson, H. Parker, S. M. Cohen, and C. L. Lee, J. Chem. Phys. **68**, 2861 (1978).

[5] C. J. Jameson, A. K. Jameson, and H. Parker, J. Chem. Phys. **68**, 2868 (1978).

[6] A. K. Jameson, J. Moyer, and C. J. Jameson, J. Chem. Phys. **68**, 2873 (1978).

[7] C. J. Jameson, A. K. Jameson, and H. Parker, J. Chem. Phys. **69**, 1318 (1978).

[8] C. J. Jameson and A. K. Jameson, J. Chem. Phys. **59**, 1655 (1978).

[9] C. J. Jameson, A. K. Jameson, and S. Wille, J. Phys. Chem. **83**, 3372 (1979).

[10] W. T. Raynes and B. P. Chadburn, J. Magn. Reson. **10**, 218 (1973).

[11] K. Jackowski and W. T. Raynes, Mol. Phys. **34**, 465 (1977).

[12] A. K. Jameson, K. Schuett, C. J. Jameson, S. M. Cohen, and H. Parker, J. Chem. Phys. **67**, 2821 (1977).

[13] D. K. Hindermann and C. D. Cornwell, J. Chem. Phys. **48**, 2017 (1968).

[14] Some theoretical estimates of $(d\sigma/d\xi)$ and $(d^2\sigma/d\xi^2)$ are available in calculations in which σ has been determined for more than one internuclear separation in diatomic molecules. See, for example, CO: R. M. Stevens and M. Karplus, J. Chem. Phys. **49**, 1094 (1968); N_2: E. A. Laws, R. M. Stevens, and W. N. Lipscomb, J. Chem. Phys. **54**, 4629 (1971); H_2: T. B. Garrett and D. Zeroka, Int. J. Quantum Chem. **6**, 663 (1972), T. W. Marshall and J. A. Pople, Mol. Phys. **3**, 339 (1960); W. T. Raynes, A. M. Davies, and D. B. Cook, Mol. Phys. **21**, 123 (1971); E. Ishiguro and S. Koide, Phys. Rev. **94**, 350 (1954); D. Zeroka, J. Chem. Phys. **59**, 3835 (1973); HF: R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. **41**, 184 (1964); LiH: R. M. Stevens and W. N. Lipscomb, J. Chem. Phys. **40**, 2238 (1964).

[15] W. H. Flygare, J. Chem. Phys. **41**, 793 (1964).

[16] R. D. Amos, Mol. Phys. **35**, 1765 (1978).

[17] E. A. Laws, R. M. Stevens, and W. N. Lipscomb, J. Chem. Phys. **54**, 4269 (1971).

[18] S. I. Chan, M. R. Baker, and N. F. Ramsey, Phys. Rev. Sect. A **136**, 1224 (1964).

[19] B. Wrackmeyer, J. Magn. Reson. **27**, 345 (1977).

[20] R. M. Stevens and M. Karplus, J. Chem. Phys. **49**, 1094 (1968).

[21] I. Ozier, L. M. Crapo, and N. F. Ramsey, J. Chem. Phys. **49**, 2314 (1968).

[22] B. E. Holder and M. P. Klein, J. Chem. Phys. **23**, 1956 (1955).

[23] J. E. Kent and E. L. Wagner, J. Chem. Phys. **44**, 3530 (1966).

[24] C. H. Bradley, G. E. Hawkes, E. W. Randall, and J. D. Roberts, J. Am. Chem. Soc. **97**, 1958 (1975).

[25] J. Chatt, M. E. Fakley, R. L. Richards, J. Mason, and I. A. Stenhouse, J. Chem. Res. (S)44 (1979).

[26] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **59**, 4540 (1973).

[27] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **62**, 4224 (1975).

[28] C. J. Jameson, A. K. Jameson, and S. M. Cohen, J. Chem. Phys. **65**, 3397 (1976).

[29] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954).

[30] C. J. Jameson, A. K. Jameson, S. M. Cohen, H. Parker, D. Oppusunggu, P. M. Burrell, and S. Wille, J. Chem. Phys. (to be published).

[31] Calculated from $\chi_m = -12.0 \times 10^{-6}$ cm^3 mole^{-1}, from Landolt-Bornstein, *Zahlenwerte und Funktionen* (Springer, Berlin, 1967), Vol. II, Part 10.

[32] A. D. Buckingham, J. Chem. Phys. **36**, 3096 (1962).

[33] C. J. Jameson, J. Chem. Phys. **66**, 4977 (1977).

[34] J. V. Foltz, D. H. Rank, and T. A. Wiggins, J. Mol. Spectrosc. **21**, 203 (1966).

[35] D. H. Rank, A. G. St. Pierre, and T. A. Wiggins, J. Mol. Spectrosc. **18**, 418 (1965).