

Weak Complexes of Dinitrogen: An Approach to the ^{14}N -Nuclear Quadrupole Coupling Constant of Free N_2 *

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The ^{14}N -nuclear quadrupole coupling constants $\chi_{aa}(^{14}\text{N}_{(2)})$ and $\chi_{aa}(^{14}\text{N}_{(1)})$ for the ground-states of the dimers $^{14}\text{N}_{(2)}^{14}\text{N}_{(1)} \cdots \text{HCCH}$ and $^{14}\text{N}_{(2)}^{14}\text{N}_{(1)} \cdots \text{HC}^{15}\text{N}$ have been corrected for zero-point effects and for the electrical effects of the subunit HX to give two estimates $\chi(^{14}\text{N}) = -5.01(13)$ and $-5.07(8)$ MHz, respectively, for the coupling constant of the isolated $^{14}\text{N}_2$ molecule.

1. Introduction

When molecules become involved in intermolecular complexes their properties undergo modification. One group of properties of particular interest in microwave spectroscopy consists of the electric field gradients at the nuclei, since these are directly related to the nuclear quadrupole coupling constants. We have recently been interested in the deconvolution of two effects that combine to modify the nuclear quadrupole coupling constants of a molecule when it becomes involved in a weakly bound dimer. The two effects in question are the zero-point motion in the dimer and the change in the electric field gradient at the nucleus of interest resulting from the approach of the other subunit.

The linear complexes of dinitrogen $\text{N}_2 \cdots \text{HX}$ where $\text{X} = \text{CN}$ or CCH present a favourable opportunity to separate the two modifying effects because of their simplicity and also because in the free dinitrogen molecule both ^{14}N -nuclear quadrupole coupling constants $\chi_0(^{14}\text{N})$ are equal. The simplicity facilitates a description of the zero-point effects while the difference in the χ values for the two nitrogen nuclei in $\text{N}_2 \cdots \text{HX}$ can arise only from the electrical effects due to HX. A comparison of $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$ is advantageous because in the former the HCCH subunit is nonpolar and the zero-point motion is expected to make the largest contribution while in the latter the effects of changes in electric field

gradient (efg) due to HCN are expected to be more significant. In this paper, we draw together some recent experimental observations for $\text{N}_2 \cdots \text{HCCH}$ [1] with the extensive and precise set of spectroscopic constants for $\text{N}_2 \cdots \text{HCN}$ [2]. The deconvolution of the two contributions to the modified χ 's is then effected by a combination of (i) *ab initio* calculations of the efg's and (ii) an empirical analysis of the zero-point motion of the N_2 subunits to give a new and well determined value of $\chi_0(^{14}\text{N})$ for free $^{14}\text{N}_2$ in the gas phase, a quantity that is difficult to obtain with precision by other means.

2. Experimental

The experimental ^{14}N -nuclear quadrupole coupling constants $\chi_{aa}(^{14}\text{N}_{(1)})$ and $\chi_{aa}(^{14}\text{N}_{(2)})$ for $\text{N}_{(2)}\text{N}_{(1)} \cdots \text{HX}$ where $\text{X} = \text{CCH}$ and CN were determined by pulsed-nozzle, Fourier-transform microwave spectroscopy using the methods outlined elsewhere [1, 2]. The values of $\chi_{aa}(^{14}\text{N}_{(m)})$ for various isotopomers of $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$ are collected in Table 1 for convenience. We shall refer

Table 1. Ground-state ^{14}N -nuclear quadrupole coupling constants $\chi_{aa}(^{14}\text{N})$ in isotopomers of the linear molecules $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HC}^{15}\text{N}$.

Isotopomer	$\chi_{aa}(^{14}\text{N}_{(2)})/\text{MHz}^a$	$\chi_{aa}(^{14}\text{N}_{(1)})/\text{MHz}^a$
$^{14}\text{N}_2 \cdots \text{HCCH}^b$	-4.213 (171)	-4.136 (176)
$^{14}\text{N}^{15}\text{N} \cdots \text{HCCH}^b$	-4.229 (2)	...
$^{15}\text{N}^{14}\text{N} \cdots \text{HCCH}^b$...	-4.162 (2)
$^{14}\text{N}_2 \cdots \text{HC}^{15}\text{N}^c$	-4.737 (15)	-4.511 (15)
$^{14}\text{N}^{15}\text{N} \cdots \text{HC}^{15}\text{N}^c$	-4.728 (1)	...
$^{15}\text{N}^{14}\text{N} \cdots \text{HC}^{15}\text{N}^c$...	-4.5438 (9)

^a The nitrogen nuclei are labelled $\text{N}_{(2)}\text{N}_{(1)} \cdots \text{HX}$ in the dimers $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$. ^b Ref. [1]. ^c Ref. [2].

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mainly to the isotopomers $^{14}\text{N}_2 \cdots \text{HC}^{15}\text{N}$ and $^{14}\text{N}_2 \cdots \text{HCCH}$.

3. Method

Rotational spectroscopy has established [1, 2] that the dimers $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$ are linear at equilibrium and the order of the nuclei is as shown, with a hydrogen bond from HX to N_2 . The distances $r(\text{N} \cdots \text{H})$ have been established as 2.604 Å and 2.552 Å, respectively, for $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$. The observed ^{14}N -nuclear quadrupole coupling constants $\chi_{aa}(^{14}\text{N}_n)$ in Table 1 refer to the zero-point state of these linear molecules and the relative changes in moments of inertia on isotopic substitution establish unambiguously the assignment of the χ_{aa} values to the particular nuclei indicated.

In a linear dimer involving N_2 , the observed zero-point constants $\chi_{aa}(^{14}\text{N}_{(n)})$ will be the resultant of three contributions, namely the value $\chi_0(^{14}\text{N})$ of the coupling constant along the molecular axis z of the isolated dinitrogen molecule, the modification of the efg at each nucleus arising from the presence of the other subunit, and the zero-point motion of the two subunits. In fact, it is known that nuclear quadrupole coupling constants associated with a subunit in a weakly bound dimer are often only slightly changed from the free molecule [3–6]. We propose therefore to treat the effects of the electrical interaction and the zero-point motion as separable here.

The first target is to establish values for the ^{14}N -nuclear quadrupole coupling constants appropriate to the linear equilibrium forms $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$. We shall then correct for the perturbation of the efg's at the nuclei $\text{N}_{(2)}$ and $\text{N}_{(1)}$ by HX .

3.1 Correction for the Zero-Point Motion

The measured nuclear quadrupole coupling constants $\chi_{aa}(^{14}\text{N}_{(1)})$ and $\chi_{aa}(^{14}\text{N}_{(2)})$ refer to averages over the zero-point state. We define the angle between the axis (z) of dinitrogen and the instantaneous principal inertial axis a of $\text{N}_2 \cdots \text{HX}$ as α , (see Figure 1). In the vibrationless, equilibrium arrangement we define the coupling constants for the nitrogen nuclei in the N_2 subunit as $\chi_e(^{14}\text{N}_{(1)})$ and $\chi_e(^{14}\text{N}_{(2)})$. These will in general be different because of the presence of HX nearby along the axis z . For present purposes, we describe the zero-point motion of the dimer in terms

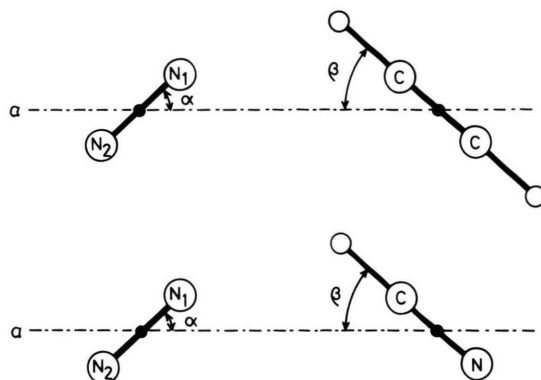


Fig. 1. Definition of the angles α and β in $\text{N}_2 \cdots \text{HCCH}$ and $\text{N}_2 \cdots \text{HCN}$.

of the angular oscillations α and β of the subunits N_2 and HX about their respective mass centres. The observed coupling constants $\chi_{aa}(^{14}\text{N}_{(n)})$ are then given in sufficient approximation by

$$\chi_{aa}(^{14}\text{N}_{(n)}) = \frac{1}{2} \chi_e(^{14}\text{N}_{(n)}) \langle 3 \cos^2 \alpha - 1 \rangle. \quad (1)$$

An effective value α_{av} of α for use in (1) to obtain $\chi_e(^{14}\text{N}_{(n)})$ is found from the average $\langle \cos \alpha \rangle$. This quantity is available in turn from the principal-axis r_s -coordinates a_1 and a_2 of the nitrogen nuclei in the dimer with the aid of

$$|a_1 - a_2| = r_s \langle \cos \alpha \rangle \quad (2)$$

in which it is assumed that the r_s -distance of free N_2 survives dimer formation. Details of the method are given elsewhere [6]. The results are $\alpha_{av} = \cos^{-1} \langle \cos \alpha \rangle = 19.7^\circ$ and 14.5° for $^{14}\text{N}_2 \cdots \text{HCCH}$ and $^{14}\text{N}_2 \cdots \text{HCN}$, respectively. Using these in (1) together with the $\chi_{aa}(^{14}\text{N}_{(n)})$ from Table 1, we find the mean values $\frac{1}{2} [\chi_e(^{14}\text{N}_{(1)}) + \chi_e(^{14}\text{N}_{(2)})]$ of the equilibrium coupling constant to be -5.03 MHz for $^{14}\text{N}_2 \cdots \text{HCCH}$ and -5.104 MHz for $^{14}\text{N}_2 \cdots \text{HC}^{15}\text{N}$. We note from Table 1 that while the mean nuclear quadrupole coupling constants in these two molecules are well determined, the differences are less so, especially for $^{14}\text{N}_2 \cdots \text{HCCH}$ [1].

3.2 Correction for Electrical Effects

At the equilibrium geometry of a dimer $\text{N}_2 \cdots \text{HX}$, the efg at a nucleus of the N_2 subunit differs from its value in the isolated molecule because of the interaction of the two monomers. There exist empirical [3] and *ab-initio* based [4] models for these differences,

and both assume that the interaction can be described by the long range intermolecular forces, in general, and by the electrostatic contribution, in particular. The latter affects the efg at a nucleus in two ways: first, through the direct efg arising from the charges of HX and, secondly, through the efg induced in the nitrogen electron cloud in response to the HX charges. The second term is a generalisation of Sternheimer shielding/antishielding effects and has been discussed in detail elsewhere [7]. Both effects are, however, captured in an *ab-initio* calculation of the supermolecule type. One such calculation has been described for $N_2 \cdots HCCH$ [1] and another, for $N_2 \cdots HCN$, is reported here.

Calculations for $N_2 \cdots HCN$ were carried out with polarised basis sets $(10s6p4d/6s4p) \rightarrow [5s3p2d/3s2p]$ [8] at the SCF level of theory using the Exeter version of the SYSMO program [9]. Total energies, electric dipole moment and efg's were calculated for collinear approach of the rigid monomers N_2 and HCN frozen at their experimental geometries. To avoid numerical problems, a threshold of 10^{-4} was applied to the overlap matrix in this diffuse basis, resulting in truncation from 113 to 111 MO's. The calculated properties are presented for a range of monomer separations $r(N \cdots H)$ in Figure 2. The essential features of the curves are qualitatively similar to those reported for $N_2 \cdots HCCH$ [1]. The energy curve exhibits a minimum at $r(N \cdots H) \cong 5 a_0$ (2.65 \AA), which should be compared with the experimental quantity 2.552 \AA . Some difference between theory and experiment is to be expected here because the calculation neglects electron correlation (dispersion) contributions to the energy. The electric dipole moment curve shows a steady increase in induced moment as the monomers come together and the interaction results in an enhancement of $0.105 e a_0$ (0.27 D) at equilibrium. The efg's in the nitrogen subunit show the qualitative trend anticipated from the experimental results, namely a fall in the magnitude of the efg at the inner nitrogen $N_{(1)}$ while that at $N_{(2)}$ rises. We note that the average efg rises in magnitude by only 0.6% as the monomers come from infinite to equilibrium separation. (In the basis set used, the efg at N in isolated N_2 is $-1.086 E_h/e a_0^2$). Also shown in Fig. 2 is the variation of efg at N in HCN. This quantity also changes by only approx. 1% over the range of $r(N \cdots H)$.

At $r(N \cdots H) = 5 a_0$, the supermolecule calculation leads to $q_{zz}(N_{(1)}) = -1.1237$ and $q_{zz}(N_{(2)}) = -1.0623 E_h/e a_0^2$, corresponding to χ values of -5.413 and

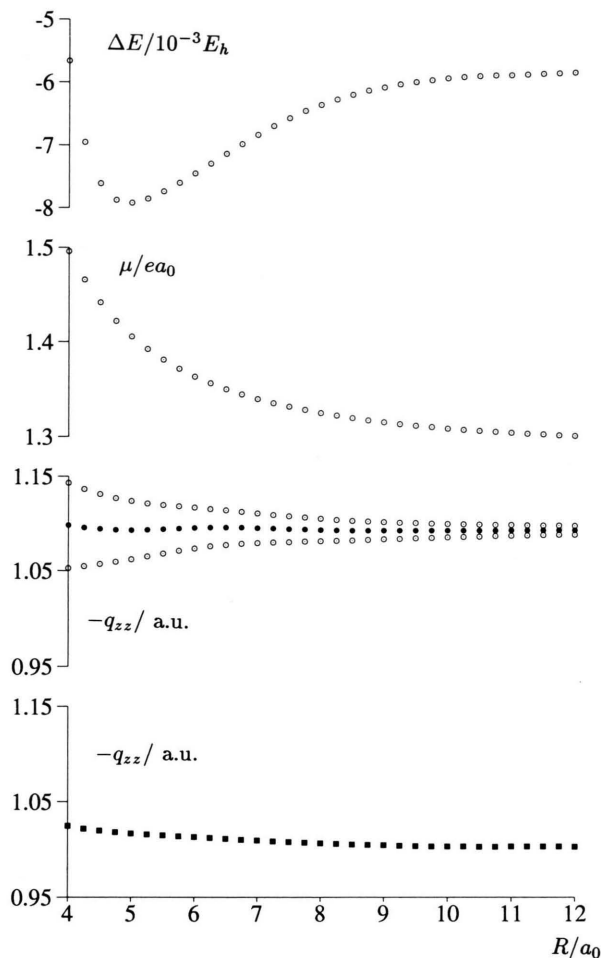


Fig. 2. Computed property curves for $N_2 \cdots HCN$. R is the $N \cdots H$ distance, ΔE is $E_{SCF} + 201.86 E_h$, μ is the total dipole moment and q_{zz} is the electric field gradient. A positive dipole corresponds to the polarity $N^+ \cdots HCN^-$. In the efg plots full circles denote the mean for inner and outer nitrogens, the upper (lower) curve is for outer (inner) N and full squares are for N in the HCN moiety. Atomic units are used for all quantities.

-5.117 MHz , respectively*. The calculation therefore predicts that formation of the dimer $^{14}N_2 \cdots HC^{15}N$ results in a rise in χ_e at $N_{(1)}$ of 0.114 MHz and a fall in χ_e at $N_{(2)}$ of 0.182 MHz , and hence to a change in the mean $\chi_e(^{14}N)$ value of only 0.034 MHz . The smallness of this change illustrates the virtue of the approach employed here, for it is exactly the mean of the

* Using the value $Q(^{14}N) = +2.05 \pm 0.02 \text{ fm}^2$ [10], a change of 1 a.u. of efg ($\sim 9.717365 \times 10^{21} \text{ Vm}^{-2}$) corresponds to a change in quadrupole coupling constant $\chi(^{14}N) = -eQ(^{14}N)q_{zz}$ of -4.817 MHz .

nitrogen coupling constants that is well determined experimentally, and this quantity is hardly changed by the electric effects. The calculation predicts a difference in coupling constant of 0.30 MHz between $N_{(1)}$ and $N_{(2)}$ in the equilibrium geometry of the complex. The experimental value, after correction for zero-point effects, is 0.25 MHz.

The quantitative changes in efg can be understood in terms of the efg response tensors. In first approximation, the shift in mean efg is a response to the applied electric field gradient while the difference in efg at the two nitrogen nuclei is a response to the applied electric field [1]. Dispersion effects, necessarily neglected in an SCF calculation, are of shorter range than electrostatic/inductive contributions and are not expected to be important for the efg [1].

Similar reasoning based on the SCF calculation for $N_2 \cdots HCCH$ [1] leads to an electrical correction of 0.02 MHz to the mean $\chi_e(^{14}N)$ and to an induced difference of 0.16 MHz between the coupling constants of the inner and outer nitrogen nuclei. We note that the change in the mean, and the induced difference, are smaller when N_2 is complexed with the non-polar acetylene than with the polar hydrogen cyanide molecule.

3.3 The ^{14}N -Nuclear Quadrupole Coupling Constant of Dinitrogen

We can now combine the experimental value of the mean equilibrium coupling constants for N_2 in each of the complexes $N_2 \cdots HCCH$ and $N_2 \cdots HCN$ with the (small) theoretical corrections for electrical effects due to the HX to give two independent estimates of the ^{14}N -nuclear quadrupole coupling constant $\chi_0(^{14}N)$ of the isolated dinitrogen molecule. From $^{14}N_2 \cdots HCCH$, we obtain -5.01 (13) MHz and from $^{14}N_2 \cdots HC^{15}N$ -5.07 (8) MHz, where the assigned error is that generated by assuming an error of one degree in the angle α_{av} in each case. It is pleasing that the two estimates are identical within the error assigned to our procedure. We note that the χ_e so obtained compare with -5.39 (5) MHz for solid α -nitrogen from NQR measurements after correction for librational motion [11], with -5.49 (18) MHz from *ab-initio* calculations [12], with the value -5.0 MHz implied for N_2 in a proposal in connection with the Townes-Dailey model by Gordy and Cook [13], and with a value near to -5.0 MHz obtained by extrapolation of molecular beam measurements for $N_2(A^3\Sigma)$ to r_e for the $X^1\Sigma$ state [14].

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