Nuclear quadrupole hyperfine structure in the rotational spectra of HCCH–N_2O and Ar–N_2O

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Hyperfine structure in N_2O-containing weakly bound complexes is fully analysed for the first time in the rotational spectra of HCCH–N_2O and Ar–N_2O using a pulsed molecular beam Fourier-transform microwave spectrometer; the nuclear quadrupole coupling constants for the two ^{14}N nuclei indicate that while Ar affects slightly the electric field gradients surrounding the nitrogen nuclei during complexation with N_2O, HCCH changes the charge distribution surrounding the central nitrogen nucleus in the HCCH–N_2O complex significantly; thus, the use of nuclear quadrupole coupling constants to obtain angular information may not be acceptable for complexes in which the field gradient of the quadrupolar nucleus is distorted in the presence of another molecule.

The determination of the structure of a weakly bound complex is primarily accomplished by the analysis of its rotational constants. However, these constants may not be sufficient to provide all the necessary geometric parameters. Further structural information may be obtained if a quadrupolar nucleus is present in the complex. The resulting hyperfine structure in the rotational spectrum provides nuclear quadrupole coupling constants which in turn give angular information (both structural and dynamical) for the complex as well as information concerning the electronic environment surrounding the quadrupolar nucleus. The hyperfine structure may become complicated when more than one quadrupolar nuclei are present in the complex.

The isoelectronic species N_2O and CO_2 have many similar and yet some different properties. We are interested in detecting how these differences are reflected in intermolecular interactions; thus, we have begun a series of investigations of N_2O-containing complexes. Such complexes have not been extensively studied in the microwave, presumably because the presence of two quadrupolar ^{14}N nuclei, and in particular, the small quadrupole coupling constant due to the central nitrogen nucleus make resolving the hyperfine components a challenge and analysing the spectrum cumbersome. In fact, as far as we are aware, merely one study, that of H_2O–N_2O,[1] has reported nuclear quadrupole coupling constants due to the nitrogen nuclei. In that work, only one component, eQq_{aa}, for each nucleus was determined, each with an uncertainty of 35%.

The complex HCCH–N_2O was first observed in the IR by Hu *et al.*[2] and was found to be planar with the subunits parallel to each other. To obtain ground-state spectroscopic constants to greater accuracy and, in particular, the quadrupole coupling constants due to the nitrogen nuclei, our work utilizes a Fourier-transform microwave spectrometer operating in the 8–16 GHz region with the pulsed molecular beam generated by a 0.8 mm diameter nozzle coaxial with the cavity axis. The complex is formed by expanding a mixture of 1% HCCH and 2% N_2O in Ar under a stagnation pressure of 4–5 atm. Fifteen rotational transitions are observed, of which six are a-type and nine are b-type. The sensitivity and resolution of the spectrometer allow us to observe over 100 hyperfine components in the transitions. The spectrum is analysed using a Watson *S*-reduced Hamiltonian with the inclusion of hyperfine interactions. The rotational and centrifugal distortion constants are listed in Table 1, together with the values reported in the IR study.[2] These constants are indeed consistent with the structure obtained in the previous work. The components of the nuclear quadrupole coupling tensor, eQq_{aa}, eQq_{bb} and eQq_{cc}, due to each nitrogen nucleus are listed in Table 2.

Additional angular information is available from the quadrupole coupling tensor of the complex. It is common practice to assume that the components of the tensor for a complex are projections of those for the monomer, which, in our case, translates as

$$eQq_{bb}(\text{complex}) = \frac{3\langle\cos^2\theta\rangle - 1}{2}\, eQq_{zz}(N_2O)$$

where θ is the angle between the *b*-axis of the complex and the N_2O axis. The quadrupole coupling constants along the molecular axis, $eQq_{zz}(N_2O)$, due to each of the two nitrogen nuclei in the free N_2O molecule have been determined by Reinartz *et al.*[3] The interpretation of quadrupole coupling constants in terms of angular properties using equations such as the one above, as pointed out by Hutson,[4] is an approximation and could lead to substantial errors for some complexes. However, the ratio $eQq_{bb}(\text{complex})/eQq_{zz}(N_2O)$ should represent $(3\langle\cos^2\theta_{\text{eff}}\rangle - 1)/2$, where θ_{eff} is an effective angle in an appropriate axis system. Hutson has also examined the *J*- and K_a-dependence of quadrupole coupling constants which we do not observe within experimental uncertainty. Because N_2O is linear, the values for θ_{eff} calculated respectively from the properties of the terminal and central nitrogen nuclei must be the same regardless of the axis system used in making the

Table 1 Rotational and centrifugal distortion constants (in MHz) of HCCH–N_2O[a]

	This work	Hu *et al.*[2]
A	9394.26826(22)	9386.60(127)
B	2831.85639(8)	2829.63(25)
C	2168.07804(7)	2166.63(21)
D_J	0.012289(3)	
D_{JK}	0.056767(40)	
d_1	−0.003365(2)	
d_2	−0.000727(10)	

[a] 1σ standard deviations in the parameters are given in parentheses.

Table 2 Components of the nuclear quadrupole coupling tensor (in MHz) for HCCH–N_2O and Ar–N_2O[a]

Constant	HCCH–N_2O	Ar–N_2O
Terminal nitrogen nucleus		
eQq_{aa}	0.3775(4)	0.3705(8)
eQq_{bb}	−0.7731(4)	−0.7592(7)
eQq_{cc}	0.3956(4)	0.3887(7)
Central nitrogen nucleus		
eQq_{aa}	0.0842(9)	0.1190(19)
eQq_{bb}	−0.2466(7)	−0.2594(12)
eQq_{cc}	0.1624(7)	0.1404(12)

[a] 1σ standard deviations in the parameters are given in parentheses.

projection. In other words, the values for θ, although they may not represent the angle between the *b*-axis of the complex and the N_2O axis, and likewise the values of the ratio eQq_{bb}(complex)/eQq_{zz}(N_2O), must be the same regardless of which ^{14}N nucleus is used to provide the quadrupole coupling constants for the calculation. Our result is surprising: the values for θ (or more accurately, $\cos^{-1} \sqrt{\langle \cos^2\theta \rangle}$) are found to be 1.4 ± 0.5 and 13.2 ± 0.2° [those of eQq_{bb}(complex)/eQq_{zz}(N_2O) are 0.9991 ± 0.0006 and 0.9217 ± 0.0027] using the constants for the terminal and central nitrogen nuclei respectively. These two angles (or eQq ratios) certainly do not agree within experimental uncertainty, and therefore we need to better understand how to obtain angular information from ^{14}N quadrupole coupling constants in N_2O-containing complexes.

A search of the literature reveals a lack of spectroscopic data to address this issue, even for the simplest N_2O-containing complex, Ar–N_2O, where N_2O is bound to a structureless Lewis base. The only microwave study of Ar–N_2O was performed by the Klemperer group.[5] Despite extensive signal averaging, the hyperfine components were difficult to resolve, thus rendering them unassignable. As a result, we decided to revisit Ar–N_2O to unravel the hyperfine structure and the quadrupole coupling constants.

Ar–N_2O is formed by expanding 4% N_2O in Ar through the pulsed nozzle under a stagnation pressure of 5 atm. To date, we have observed a total of 16 rotational transitions, of which five are a-type and eleven are b-type, and of which nine were not previously observed by the Klemperer group. The analysis of nine transitions (1_{11}–0_{00}, 1_{10}–1_{01}, 2_{02}–1_{01}, 4_{13}–4_{04}, 4_{23}–5_{14}, 5_{05}–4_{14}, 5_{14}–5_{05}, 6_{06}–5_{15} and 7_{07}–6_{16}) allows the determination of the quadrupole coupling constants due to each nitrogen nucleus, as listed in Table 2. Angular information is again determined using eQq_{bb}(complex) and eQq_{zz}(N_2O). The values for θ are found to be 6.4 ± 0.2 and 8.2 ± 0.6° [whereas the values of the ratio eQq_{bb}(complex)/eQq_{zz}(N_2O) are 0.9812 ± 0.0008 and 0.9694 ± 0.0040] using the terminal and central nitrogen nuclei respectively. These two angles and ratios are much more similar, unlike the case for HCCH–N_2O.

To further understand the relation between the quadrupole coupling constants for the Ar–N_2O complex and the N_2O monomer, it is instructive to compare eQq_{cc}(complex) with eQq_{xx}(N_2O) which is simply $-eQq_{zz}$(N_2O)/2 (386.88 kHz for the terminal and 133.79 kHz for the central nitrogen nucleus). Because the complex formed between an atom and a linear molecule must be planar, its *c*-axis is parallel with the *x*-axis of the N_2O monomer. Hence eQq_{cc}(complex) should be equal to eQq_{xx}(N_2O). Indeed, eQq_{cc} differs from eQq_{xx} by 0.5 ± 0.2% for the terminal and 4.9 ± 0.9% for the central nitrogen nuclei. The closeness of these percentages implies that the use of quadrupole coupling constants to give angular information is approximately valid for Ar–N_2O, and that argon does not affect the field gradients around the two nitrogen nuclei greatly. The Ar–N_2O work is ongoing and we are in the process of observing more transitions. The analysis of all the data will allow the determination of rotational constants, centrifugal distortion constants, and quadrupole coupling constants to greater accuracy.

The planarity of HCCH–N_2O indicates that eQq_{cc}(complex) should also be equal to eQq_{xx}(N_2O). Indeed, the two eQq values differ by only 2.3 ± 0.1% for the terminal nitrogen nucleus, but by 21.4 ± 0.5% for the central nitrogen nucleus. Clearly, the field gradient surrounding the central nitrogen nucleus is distorted due to the presence of HCCH and therefore eQq_{bb} for this nucleus will not give correct angular information. The field gradient of N_2O may be affected by a variety of factors: the charge distribution of HCCH, electrical moments induced in N_2O, and a deviation from linearity of the N_2O in the complex; each will be examined more thoroughly in a full paper.

In conclusion, our work on two N_2O complexes indicates that the analysis of hyperfine structure, although requiring some effort, supplies important information of how one molecular subunit is affected by its binding partner. We find that (*i*) as commonly suggested, quadrupole coupling constants may be appropriate in determining angular information for a weakly bound complex, although the relationship between the two may be more complicated as described by Hutson;[4] (*ii*) in cases where the charge distribution surrounding the quadrupolar nucleus may be affected by the presence of another molecule, caution must be taken in employing quadrupole coupling constants to interpret angular information; and (*iii*) hyperfine structure reveals a wealth of information not only on complex geometry and dynamics, but also on the nature of intermolecular interactions.

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Footnote

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References

1 D. Zolandz, D. Yaron, K. I. Peterson and W. Klemperer, *J. Chem. Phys.*, 1992, **97**, 2861.
2 T. A. Hu, L. H. Sun and J. S. Muenter, *J. Chem. Phys.*, 1991, **95**, 1537.
3 J. M. J. L. Reinartz, W. L. Meerts and A. Dymanus, *Chem. Phys.*, 1978, **31**, 19.
4 J. M. Hutson, *Mol. Phys.*, 1995, **84**, 185.
5 C. H. Joyner, T. A. Dixon, F. A. Baiocchi and W. Klemperer, *J. Chem. Phys.*, 1981, **75**, 5285.

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