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Citation: The Journal of Chemical Physics **84**, 5711 (1986); doi: 10.1063/1.449930
View online: https://doi.org/10.1063/1.449930
View Table of Contents: http://aip.scitation.org/toc/jcp/84/10
Published by the American Institute of Physics

Nitrogen quadrupole coupling constants for HCN and H_2CN^+: Explanation of the absence of fine structure in the microwave spectrum of interstellar H_2CN^+

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(Received 14 January 1986; accepted 7 February 1986)

Nitrogen 14 quadrupole coupling constants for H_2CN^+ and HCN are predicted via *ab initio* self-consistent-field and configuration interaction theory. Effects of electron correlation, basis set completeness, and geometrical structure on the predicted electric field gradients are analyzed. The quadrupole coupling constant obtained for H_2CN^+ is one order of magnitude less than in HCN, providing an explanation for the experimental fact that the fine structure of the microwave spectrum of H_2CN^+ has not been resolved. This research also allows a reliable prediction of the nuclear quadrupole moment of ^{14}N, namely $Q(^{14}N) = 2.00 \times 10^{-26}$ cm^2.

INTRODUCTION

Despite the fact that $HCNH^+$ has a small permanent dipole moment,[1–4] the microwave spectrum of this molecular ion has very recently been observed in interstellar space. Ziurys and Turner[5] observed the $J = 1$–0, 2–1, and 3–2 rotational transitions of $HCNH^+$ toward Sgr. B2 between October 28, 1984 and April 16, 1985. The laboratory millimeter and submillimeter wave spectrum of $HCNH^+$ was also recently detected by Bogey, Demuynck, and Destombes.[6] In this work we report *ab initio* values of the ^{14}N nuclear quadrupole coupling constants (QCC) for HCN and $HCNH^+$. Theoretical predictions of vibrational frequencies and infrared intensities for protonated HCN were the subject of a previous paper.[1]

Normally, the microwave spectrum of a molecule which contains an atom with a nuclear quadrupole moment will exhibit fine structure due to the electric interaction between the nuclear quadrupole moment and the electric field gradient at the nucleus. However, it was emphasized by Ziurys and Turner[5] that fine structure could not be resolved for $HCNH^+$; the implication being that the electric field gradient at the ^{14}N nucleus of $HCNH^+$, and hence the QCC, was very small. Thus we decided to predict the *ab initio* electric field gradient and corresponding ^{14}N QCC for $HCNH^+$. To our knowledge the present research represents perhaps the first thorough examination of the effects of electron correlation on predicted nitrogen quadrupole coupling constants.

THEORETICAL APPROACH

Nuclear quadrupole coupling constants may be obtained from the *ab initio* molecular electric field gradient (q) if the nuclear quadrupole moments (Q) are known. Numerous *ab initio* predictions of electric field gradients have been reported for deuterium[7] and for ^{14}N containing molecules.[8–27] The Hamiltonian representing the interaction between the nuclear quadrupole moment and the electronic electric field gradient may be written as[28,29]

$$H = e^2 \sum_{j,A} \frac{Q_A}{2I_A(2I_A - 1)} [I_A^2 r_{jA}^2 - 3(\bar{r}_{jA} \cdot \bar{I}_A)^2]/r_{jA}^5, \tag{1}$$

where I_A is the nuclear spin of nucleus A ($I_A \geqslant 1$ is required for Q_A to be different from zero), and $r_{jA} = |\bar{r}_j - \bar{R}_A|$ is the distance between electron j and nucleus A. The total electric field gradient is a second-rank tensor whose components at the site of nucleus A are

$$q_A^{\alpha\beta} = \sum_{\mu\nu} P_{\mu\nu} \langle \phi_\mu | (r_A^2 \delta_{\alpha\beta} - 3 r_{A\alpha} r_{A\beta})/r_A^5 | \phi_\nu \rangle + \sum_{B \neq A} Z_B (3 R_{AB\alpha} R_{AB\beta} - \delta_{\alpha\beta} R_{AB}^2)/R_{AB}^5, \tag{2}$$

where $\alpha, \beta = x, y$, and z; $P_{\mu\nu}$ is the reduced one-particle density matrix; ϕ_μ, ϕ_ν are atomic orbitals and $R_{AB} = |\bar{R}_A - \bar{R}_B|$ are internuclear distances. Also in Eq. (2), r_A is the distance of the electron from nucleus A; $r_{A\alpha}$ is the difference in Cartesian coordinate α (i.e., x, y, or z) between the electron and nucleus A; and $R_{AB\alpha}$ is the difference in Cartesian coordinate α between nucleus A and nucleus B. The two terms in Eq. (2) correspond to the electronic and nuclear contributions, respectively. For linear molecules the QCC is straightforwardly obtained as $e^2 q_N^{zz} Q_N/h$, with z being the axis of the molecule.

One-particle density matrices were obtained for both the self-consistent-field (SCF) and configuration interaction (CI) wave functions and subsequently used in the evaluation of the electronic contribution to the electric field gradient [see Eq. (2)]. The electric field gradient integrals over the atomic orbital basis were evaluated using standard techniques.[30]

Initially the electric field gradient was evaluated with SCF wave functions in conjunction with the standard Huzinaga–Dunning[31,32] double zeta plus polarization (DZ + P) basis used previously.[1] This basis is designated (9*s*5*p*1*d* /4*s*2*p*1*d*) for the heavy atoms (C and N) and (4*s*1*p*/2*s*1*p*) for H. The hydrogen *s* functions were scaled by a fac-

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 0021-9606/86/105711-04$02.10

TABLE I. Predicted equilibrium geometries and energies for HCN and protonated HCN.

	H_2CN^+		HCN	
Bond length (Å)	SCF	CISD	SCF	CISD
HN	1.006	1.015	...	...
NC	1.121	1.144	1.136	1.163
CH	1.076	1.080	1.062	1.068
Energies (a.u.)	− 93.176 98	− 93.446 27	− 92.889 89	− 93.160 48

tor of 1.2, and the polarization function exponents were $\alpha_d(C) = 0.75$, $\alpha_d(N) = 0.8$, and $\alpha_p(H) = 1.0$.

Correlation effects were analyzed by way of CI wave functions including all single and double excitations with respect to the SCF reference function with the exceptions that the C_{1s}- and N_{1s}-like orbitals were kept doubly occupied and the corresponding orbitals deleted from the virtual space. The SCF DZ + P and CISD DZ + P optimized geometries were taken from the literature[1] and are given in Table I for completeness.

The influence of the basis was investigated by using the less contracted triple zeta (TZ) Huzinaga–Dunning basis,[33] the (11*s*6*p*) and (13*s*8*p*) primitive set of van Duijneveldt[34] for C and N, and the 6*s*, 8*s*, and 10*s* primitive sets of the same author[34] for hydrogen. All contractions of these basis sets were performed over the innermost primitives.

The polarization function orbital exponents given above were used when one set of polarization functions was added to these *sp* basis sets. However, the quadrupole coupling constants were also evaluated using basis sets including two sets of polarization functions on each atom. When two sets were added the polarization exponents were $\alpha_p = 1.2$ and 0.4 for H, $\alpha_d = 1.5$ and 0.5 for N, and $\alpha_d = 1.2$ and 0.4 for C.

RESULTS AND DISCUSSION

In Table I, the predicted equilibrium geometries and the corresponding energies for both HCN and protonated HCN, evaluated with SCF and CI wave functions, are presented. As usual, CI bond lengths are longer than the SCF ones.

The ^{14}N QCC for HCN has been measured by DeLucia and Gordy,[35] the experimental value being − 4.7091 ± 0.0013 MHz. The nuclear quadrupole moment of ^{14}N has recently been deduced by Ha[25] to be 1.95×10^{-26} cm^2. Therefore, theoretical values of the electric field gradient may be used to test the accuracy of theoretical predictions for the QCC, by way of combination with known or estimated nuclear quadrupole moments. On the other hand, theoretical values of the electric field gradient may be used to predict the quadrupole moment at a determined level of theory, provided the experimental QCC are known. In this paper, we have initially used Ha's suggested value of the ^{14}N quadrupole moment to predict the QCC for H_2CN^+.

In Table II we report the basis set dependence of the electric field gradients of HCN and H_2CN^+ at the SCF level of theory. These calculations were carried out at the corresponding CISD DZ + P optimized geometries (see Table

TABLE II. Energies, electric field gradients, and nuclear quadrupole coupling constants of ^{14}N in HCN and H_2CN^+ for different basis sets at the SCF level of theory.[a] The nuclear quadrupole moment of ^{14}N was assumed to be 1.95×10^{-26} cm^2, as proposed in Ref. 25.

	HCN			H_2CN^+		
Entry Basis	*E*(a.u.)	*q*(a.u.)	e^2Qq/h(MHz)	*E*(a.u.)	*q*(a.u.)	e^2Qq/h(MHz)
1. STO3G	− 91.674 88	− 0.341	− 1.56	− 91.996 27	0.533	2.44
2. DZ	− 92.836 41	− 0.813	− 3.72	− 93.128 16	0.152	0.70
3. TZ	− 92.845 95	− 1.110	− 5.09	− 93.137 09	0.000	0.00
4. (11*s*6*p*/8*s*4*p*)(6*s*/4*s*)	− 92.857 69	− 1.044	− 4.78	− 93.147 89	0.028	0.13
5. (13*s*8*p*/9*s*5*p*)(8*s*/6*s*)	− 92.860 29	− 1.054	− 4.83	− 93.150 35	0.018	0.08
6. (13*s*8*p*/10*s*6*p*)(10*s*/8*s*)	− 92.860 94	− 1.082	− 4.96	− 93.151 11	− 0.011	− 0.05
7. Uncontracted (13*s*8*p*)(10*s*)	− 92.860 97	− 1.076	− 4.93	− 93.151 14	− 0.006	− 0.03
8. DZ + P	− 92.888 04	− 0.936	− 4.28	− 93.175 35	0.099	0.45
9. TZ + P	− 92.896 25	− 1.133	− 5.19	− 93.183 11	− 0.123	− 0.56
10. TZ + P + P_d[b]	− 92.898 17	− 1.115	− 5.11	− 93.184 14	− 0.121	− 0.55
11. TZ + 2P	− 92.900 54	− 1.140	− 5.22	− 93.186 68	− 0.127	− 0.58
12. (13*s*8*p*1*d*/9*s*5*p*1*d*)(8*s*1*p*/6*s*1*p*)	− 92.906 94	− 1.132	− 5.19	− 93.193 99	− 0.092	− 0.42
13. (13*s*8*p*2*d*/9*s*5*p*2*d*)(8*s*2*p*/6*s*2*p*)	− 92.910 19	− 1.146	− 5.25	− 93.196 32	− 0.111	− 0.51
Experimental[c]			− 4.7091 ± 0.0013			

[a] Optimized CISD geometries with the DZ + P basis set were used (Table I).
[b] Exponents of diffuse polarization functions in the P_d set are 0.15 for all atoms.
[c] Reference 35.

TABLE III. Influence of electron correlation effects on the predicted values of electric field gradients and nuclear quadrupole coupling constants for ^{14}N in HCN and H_2CN^+.[a]

	HCN			H_2CN^+		
	E(a.u.)	q(a.u.)	e^2qQ/h(MHz)	E(a.u.)	q(a.u.)	e^2Qq/h(MHz)
DZ + P basis set						
SCF	− 92.888 04	− 0.936	− 4.28	− 93.175 35	0.099	0.45
CISD[b]	− 93.160 48	− 0.798	− 3.66	− 93.446 27	0.104	0.48
CISD[c]	− 93.188 24	− 0.804	− 3.68	− 93.474 68	0.103	0.47
TZ + 2P basis set						
SCF	− 92.900 54	− 1.140	− 5.22	− 93.186 68	− 0.127	− 0.58
CISD[b]	− 93.203 99	− 1.000	− 4.58	− 93.440 58	− 0.119	− 0.55

[a] Optimized CISD geometries with DZ + P basis sets were used (see Table I).
[b] Two innermost doubly occupied molecular orbitals and corresponding virtuals are frozen.
[c] All single and double replacements are included.

I). Without using polarization functions it is not possible to find convergence for the valence *sp* basis set. This is true even with the uncontracted C, N(13*s*8*p*) H(10*s*) set. It is apparent that polarization functions are of crucial importance for this property. We have also investigated the influence of diffuse polarization functions (see entry 10 of Table II), and such functions reduce the value of q slightly. From results presented in Table II we conclude that at least the TZ + 2P basis set should be used if quantitative agreement with experimental results is desired. Smaller basis sets are less than satisfactory. Our value for HCN with the TZ + 2P basis set at the SCF level (− 5.22 MHz) is reasonably close to the experimental value (− 4.71 MHz). In comparing these figures one should take into account the uncertainty[25] in the quadrupole moment for ^{14}N.

The influence of correlation effects is analyzed in Table III for both HCN and H_2CN^+ with DZ + P and TZ + 2P basis sets. In evaluating the electric field gradient we chose an expectation value approach.[36] This means that Eq. (2) was used for the electric field gradients, with $P_{\mu\nu}$ being now the one-particle reduced density matrix obtained from the CISD wave function. Also examined was the influence of keeping the innermost doubly occupied molecular orbitals and corresponding virtuals frozen with the DZ + P basis set and, as expected, we found it of less importance. The results presented in Table III show that in HCN correlation effects increase the predicted electric field gradient by ~0.14 a.u., or 12%–14%. The same increase holds for H_2CN^+ but to a much smaller degree, 0.004–0.008 a.u.

The influence of the assumed geometrical structure on the predicted electric field gradients and quadrupole coupling constants is another parameter to be analyzed. Such a study is reported in Table IV. Results obtained show that these properties are only somewhat sensitive to the small perturbations introduced (± 0.01 a.u. in all bond lengths with respect to the optimized CISD DZ + P structures). However, it may be concluded that neither this structural dependence nor correlation effects will affect the order of magnitude of the predicted electric field gradients and consequently the calculated ^{14}N QCC in these molecules.

Obviously, a precise quantitative prediction for the ^{14}N QCC in H_2CN^+ will require a refinement in basis set, correlation effects, and geometrical structure and is not the purpose of this paper. Nevertheless, from the results obtained in this work we may conclude that the nuclear quadrupole coupling constant for ^{14}N in H_2CN^+ is in the range of − 0.55 ± 0.3 MHz or one order of magnitude less than in HCN. This prediction satisfactorily explains the experimental observation that the fine structure of the microwave spectrum of interstellar H_2CN^+ was not resolved.[5]

CONCLUDING REMARKS

There is no meaningful purely experimental value for the nuclear quadrupole moment of ^{14}N. The most reliable values for this quadrupole moment may be obtained by com-

TABLE IV. Influence of the geometrical structure on the predicted values of electric field gradients and nuclear quadrupole coupling constants for ^{14}N in HCN and H_2CN^+ using a TZ + 2P basis set at the SCF level of theory.

	HCN			H_2CN^+		
	E(a.u.)	q(a.u.)	e^2Qq/h(MHz)	E(a.u.)	q(a.u.)	e^2Qq/h(MHz)
$+\delta$[b]	− 92.899 37	− 1.128	− 5.17	− 93.185 43	− 0.120	− 0.55
OPT CISD DZ + P[a]	− 92.900 54	− 1.140	− 5.22	− 93.186 68	− 0.127	− 0.58
$-\delta$[c]	− 92.901 54	− 1.153	− 5.28	− 93.187 72	− 0.134	− 0.61

[a] Optimized CISD structures with DZ + P basis sets (see Table I).
[b] All bond lengths are increased by 0.01 a.u. with respect to a the CI equilibrium geometry.
[c] All bond lengths are decreased by 0.01 a.u. with respect to a.

bining an *ab initio* electric field gradient with an experimental quadrupole coupling constant. The latest reports[25,27] of this type deduce from ammonia a value $Q(^{14}N) = 1.95\times10^{-26}$ cm^2 and from N_2 and NO^+ a value $Q(^{14}N) = 2.05\times10^{-26}$ cm^2.

Our most reliable theoretical value for the electric field gradient of HCN is the TZ + 2P CI value in Table III, namely -1.000 a.u. Combined with the experimental quadrupole coupling constant[35] (-4.71 MHz) for $HC^{14}N$, we deduce $Q(^{14}N) = 2.00\times10^{-26}$ cm^2. The fact that our prediction (based on the HCN molecule) is similar to those obtained in separate high-quality *ab initio* studies involving other molecules is a good indication that this is indeed a reasonable prediction for the nuclear quadrupole moment of ^{14}N.

ACKNOWLEDGMENTS

This work was supported by the U. S. National Science Foundation, Grant No. CHE-8218785. G. E. S. wishes to acknowledge financial support by CONICET, the National Research Council of Argentina. We are grateful to Dr. Lucy Ziurys for helpful discussions and the preliminary communication of her interstellar discovery (Ref. 5) of H_2CN^+.

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