Electrical Properties for HCO^+ and NNH^+ from Fourth-Order Møller-Plesset Perturbation Theory

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Z. Naturforsch. **43a**, 419–429 (1988); received February 5, 1988

Electric multipole moments and static polarizabilities are reported for HCO^+ and NNH^+. Both molecular ions are of great importance to interstellar matter chemistry. All properties were calculated from the energy of the molecule in the presence of distant electric charges. Electron correlation effects were taken into account via SDQ-MPPT(4), fourth-order Møller-Plesset Perturbation Theory with single, double and quadrupole substitutions from the reference SCF wavefunction. With the exception of the dipole moment, values for the other properties studied in this work appear in the literature for the first time. The dipole moment (relative to the centre of mass) and the axial and perpendicular components of the dipole polarizability are 1.515 ea_0, 13.39 and 6.88 $e^2a_0^2E_h^{-1}$ respectively for HCO^+ and 1.328 ea_0, 13.81 and 5.70 $e^2a_0^2E_h^{-1}$ for NNH^+.

Key words: HCO^+, NNH^+, Electric Moments, Electric Polarizabilities

I. Introduction

The molecular ions HCO^+ and NNH^+ have been detected in the interstellar gas via radio-astronomical observations supported by laboratory measurements of microwave frequencies [1]. Microwave spectroscopy has also been used for the determination of the molecular structure of these ions. Woods et al. [2] have obtained substitution molecular structures (r_s) from measurements of the $J = 0 \to 1$ transition frequency of isotopically substituted HCO^+ and NNH^+.

HCO^+ and NNH^+ have been the object of several theoretical studies. However, most of them have focused on the accurate calculation of the molecular geometry and the $J = 0 \to 1$ rotational frequency [3]. The calculation of electrical properties has been limited to the prediction of the electric dipole moment. Green et al. [4] reported a near-Hartree-Fock limit calculation of the dipole moment of NNH^+. Hillier and Kendrick [5] reported SCF and CI values for the dipole moment of NNH^+, calculated at the respective theoretical equilibrium geometries. An SCF values of the dipole moment of HCO^+ has been obtained by Woods et al. [6] while Haese and Woods calculated the same property for both HCO^+ and NNH^+ at the SCF and CI theoretical levels [7]. In their theoretical study on HCC^+ Montgomery and Dykstra [8] reported SCF and correlated values for the dipole moment of NNH^+ as well. SCF dipole moments and infrared intensities for HCO^+ were reported by Rogers and Hillman [9] while DeFrees et al. [10] calculated the dipole moment of both molecular ions at the SD-CI level (configuration interaction with single and double substitutions from the reference SCF wavefunction).

In this work we report SCF and correlated values for the dipole, quadrupole and octopole electric moments (μ, Θ and Ω), the dipole polarizability (α), the first and second dipole hyperpolarizability (β and γ), the dipole-quadrupole polarizability (A) and the dipole-dipole-quadrupole polarizability (B). We also report SCF values for the hexadecapole moment (Φ), the quadrupole polarizability (C) and the dipole-octopole polarizability (E). All properties were calculated from the energies of the molecule in the presence of the field of a distant charge. The calculation of the molecular polarizabilities from the induced electric moments, a method adopted in previous work [11], requires considerably less computational effort but its applicability is limited to wavefunctions which obey the Hellmann-Feynman theorem [12]. Electron correlation effects are taken into account via

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Møller-Plesset perturbation theory. Our approach consists in calculating the correlation correction to the perturbed energy of the molecule. The correlation correction to all properties is then extracted from the respective correction to the perturbed energy as in earlier work on Li_2 and N_2 [13]. Thus, the second, third and fourth order corrections to a given property are obtained from the respective corrections to the perturbed molecular energy.

Atomic units are used throughout this work. $1\,a_0 \simeq 0.52917706 \times 10^{-10}$ m, $1\,E_h \simeq 4.3598 \times 10^{-18}$ J, $1\,ea_0 \simeq 8.4784 \times 10^{-30}$ Cm, $1\,ea_0^2 \simeq 4.4866 \times 10^{-40}$ Cm^2, $1\,ea_0^3 \simeq 2.3742 \times 10^{-50}$ Cm^3, $1\,ea_0^4 \simeq 1.2564 \times 10^{-60}$ Cm^4, $1\,e^2a_0^2E_h^{-1} \simeq 0.16488 \times 10^{-40}$ C^2 m^2 J^{-1}, $1\,e^3a_0^3E_h^{-2} \simeq 0.32063 \times 10^{-52}$ C^3 m^3 J^{-2}, $1\,e^4a_0^4E_h^{-3} \simeq 0.62360 \times 10^{-64}$ C^4 m^4 J^{-3}, $1\,e^2a_0^3E_h^{-1} \simeq 8.7250 \simeq 10^{-52}$C^2 m^3 J^{-1}, $1\,e^2a_0^4E_h^{-1} \simeq 4.6171 \times 10^{-62}$ C^2 m^4 J^{-1} and $1\,e^3a_0^4E_h^{-2} \simeq 1.6967 \times 10^{-63}$ C^3 m^4 J^{-2}.

II. Theory

The energy of a molecular ion in a weak, general electric field can be expanded as [14, 15]

$$\begin{aligned} E = {} & E^0 + q\,\phi(0) - \mu^0_\alpha F_\alpha - \frac{1}{3}\,\Theta^0_{\alpha\beta} F_{\alpha\beta} \\ & - \frac{1}{15}\,\Omega^0_{\alpha\beta\gamma} F_{\alpha\beta\gamma} - \frac{1}{105}\,\Phi^0_{\alpha\beta\gamma\delta} F_{\alpha\beta\gamma\delta} + \dots \\ & - \frac{1}{2}\alpha_{\alpha\beta} F_\alpha F_\beta - \frac{1}{3} A_{\alpha,\beta\gamma} F_\alpha F_{\beta\gamma} \\ & - \frac{1}{6} C_{\alpha\beta,\gamma\delta} F_{\alpha\beta} F_{\gamma\delta} - \frac{1}{15} E_{\alpha,\beta\gamma\delta} F_\alpha F_{\beta\gamma\delta} + \dots \\ & - \frac{1}{6}\beta_{\alpha\beta\gamma} F_\alpha F_\beta F_\gamma - \frac{1}{6} B_{\alpha\beta,\gamma\delta} F_\alpha F_\beta F_{\gamma\delta} + \dots \\ & - \frac{1}{24}\gamma_{\alpha\beta\gamma\delta} F_\alpha F_\beta F_\gamma F_\delta + \dots\,, \end{aligned} \tag{1}$$

where E^0, μ^0, Θ^0, Ω^0 and Φ^0 are the energy and permanent electric moments of the free molecule, q its charge (the zeroth-order moment), $\phi(0)$ the perturbing potential at the origin and α, β, γ, A, C, E, and B the static electric polarizabilities. F_α, $F_{\alpha\beta}$, etc. are the electric field, field gradient, etc. at the origin. The greek subscripts denote cartesian tensor components and a repeated subscript denotes a summation over all three cartesian coordinates x, y, and z.

A linear molecule has only one independent component for any multipole moment. With z as the molecular axis we specify the multipole moment tensors by their μ^0_z, Θ^0_{zz}, Ω^0_{zzz}, and Φ^0_{zzzz} components. We specify $\alpha_{\alpha\beta}$ by α_{zz} and α_{xx}, $\beta_{\alpha\beta\gamma}$ by β_{zzz} and β_{zxx}, $\gamma_{\alpha\beta\gamma\delta}$ by γ_{zzzz}, γ_{xxxx} and γ_{xxzz}, $A_{\alpha,\beta\gamma}$ by $A_{z,zz}$ and $A_{x,zx}$, $C_{\alpha\beta,\gamma\delta}$ by $C_{zz,zz}$, $C_{xz,xz}$ and $C_{xx,xx}$, $E_{\alpha,\beta\gamma\delta}$ by $E_{z,zzz}$ and $E_{x,xxx}$ and $B_{\alpha\beta,\gamma\delta}$ by $B_{zz,zz}$, $B_{xz,xz}$, $B_{xx,zz}$ and $B_{xx,xx}$ [15, 16]. Let $E(Q, R, \theta)$ be the energy of the molecule in the presence of the static field of a distant electric charge Q with its position defined by the polar coordinates (R, θ) on the xz plane. Equation (1) is then written as [11],

$$\begin{aligned} E(Q, R, \theta) = {} & E^0 + (qQ/R) + \mu^0_z (Q/R^2)\cos\theta \\ & + \frac{1}{2}\,\Theta^0_{zz}(Q/R^3)(3\cos^2\theta - 1) \\ & + \frac{1}{2}\,\Omega^0_{zzz}(Q/R^4)(5\cos^3\theta - 3\cos\theta) \\ & + \frac{1}{24}\,\Phi^0_{zzzz}(Q/R^5)(105\cos^4\theta - 90\cos^2\theta + 9) \\ & - \frac{1}{2}\alpha_{zz}(Q^2/R^4)\cos^2\theta \\ & - \frac{1}{2}\alpha_{xx}(Q^2/R^4)\sin^2\theta \\ & - \frac{1}{2} A_{z,zz}(Q^2/R^5)\cos\theta(3\cos^2\theta - 1) \\ & - 2\,A_{x,zx}(Q^2/R^5)\cos\theta\sin^2\theta \\ & - \frac{3}{2} C_{zz,zz}(Q^2/R^6)\cos^2\theta(2\cos^2\theta - 1) \\ & - 6\,C_{xz,xz}(Q^2/R^6)\cos^2\theta\sin^2\theta \\ & - \frac{3}{2} C_{xx,xx}(Q^2/R^6)\sin^4\theta \\ & - \frac{1}{2} E_{z,zzz}(Q^2/R^6)\cos^2\theta(5\cos^2\theta - 3) \\ & + E_{x,xxx}(Q^2/R^6)\sin^2\theta(5\cos^2\theta - 1) \\ & + \frac{1}{6}\beta_{zzz}(Q^3/R^6)\cos^3\theta \\ & + \frac{1}{3}\beta_{zxx}(Q^3/R^6)\cos\theta\sin^2\theta \end{aligned}$$

$$+\frac{1}{4}B_{zz,zz}(Q^3/R^7)\cos^2\theta(3\cos^2\theta-1)$$
$$+2B_{xz,xz}(Q^3/R^7)\cos^2\theta\sin^2\theta$$
$$+\frac{1}{2}B_{xx,zz}(Q^3/R^7)\sin^2\theta\cos^2\theta$$
$$+\frac{1}{2}B_{xx,xx}(Q^3/R^7)\sin^4\theta$$
$$-\frac{1}{24}\gamma_{zzzz}(Q^4/R^8)\cos^4\theta$$
$$-\frac{1}{24}\gamma_{xxxx}(Q^4/R^8)\sin^4\theta$$
$$-\frac{1}{4}\gamma_{xxzz}(Q^4/R^8)\cos^2\theta\sin^2\theta$$
$$+\dots \quad (2)$$

From (2), the electric moments and polarizabilities are calculated as follows: Let

$$S_1(Q,R,\theta)=E(-Q,R,\theta)+E(-Q,R,\pi-\theta)+E(Q,R,\theta)+E(Q,R,\pi-\theta)\ , \quad (3)$$

$$S_2(Q,R,\theta)=E(-Q,R,\theta)-E(-Q,R,\pi-\theta)-E(Q,R,\theta)+E(Q,R,\pi-\theta)\ , \quad (4)$$

$$S_3(Q,R,\theta)=E(-Q,R,\theta)-E(-Q,R,\pi-\theta)+E(Q,R,\theta)-E(Q,R,\pi-\theta)\ , \quad (5)$$

$$S_4(Q,R,\theta)=E(-Q,R,\theta)+E(-Q,R,\pi-\theta)-E(Q,R,\theta)-E(Q,R,\pi-\theta)\ . \quad (6)$$

The dipole and octopole moments are calculated from (2) and (4).

$$DS_2(\theta)\equiv S_2(2Q,R,\theta)-8S_2(Q,R,\theta)\ ,$$
$$\mu_z^0=(R^2/30Q)(\tfrac{1}{4}DS_2(0)+2^{1/2}DS_2(\pi/4))\ , \quad (7)$$
$$\Omega_{zzz}^0=(R^4/30Q)(DS_2(0)-2^{1/2}DS_2(\pi/4))\ . \quad (8)$$

The quadrupole and hexadecapole moments are obtained from (2) and (6).

$$DS_4(\theta)\equiv S_4(2Q,R,\theta)-8S_4(Q,R,\theta)\ ,$$
$$\Theta_{zz}^0=(R^3/168Q)(3DS_4(0)-8DS_4(\pi/2)+120qQ/R)\ , \quad (9)$$
$$\Phi_{zzzz}^0=(R^5/42Q)(DS_4(0)+2DS_4(\pi/2)-72qQ/R)\ . \quad (10)$$

From (2) and (3)

$$(R^4/24Q^2)(S_1(2Q,R,0)-16S_1(Q,R,0)+60E^0)=\alpha_{zz}+3C_{zz,zz}R^{-2}+2E_{z,zzz}R^{-2}\simeq\alpha_{zz}\ , \quad (11)$$

$$(R^4/24Q^2)(S_1(2Q,R,\pi/2)-16S_1(Q,R,\pi/2)+60E^0)=\alpha_{xx}+3C_{xx,xx}R^{-2}+2E_{x,xxx}R^{-2}\simeq\alpha_{xx}\ . \quad (12)$$

The contamination of the dipole polarizability values from the contributions of the higher polarizabilities C and E depends only on R and can be made arbitrarily small by placing the charge sufficiently far from the molecule.

The components of the first dipole hyperpolarizability tensor are calculated from (2) and (4) as

$$\beta_{zzz}=(R^6/4Q^3)(2S_2(Q,R,0)-S_2(2Q,R,0))\ , \quad (13)$$

$$\beta_{zzz}+3\beta_{zxx}=(R^6/2^{1/2}Q^3)(2S_2(Q,R,\pi/4)-S_2(2Q,R,\pi/4))\ . \quad (14)$$

γ_{zzzz}, γ_{xxxx} and γ_{xxzz} are calculated from (2) and (3) as

$$\gamma_{zzzz}=(R^8/2Q^4)(4S_1(Q,R,0)-S_1(2Q,R,0)-12E^0)\ , \quad (15)$$

$$\gamma_{xxxx}=(R^8/2Q^4)(4S_1(Q,R,\pi/2)-S_1(2Q,R,\pi/2)-12E^0)\ , \quad (16)$$

$$\gamma_{zzzz}+\gamma_{xxxx}+6\gamma_{xxzz}=(2R^8/Q^4)(4S_1(Q,R,\pi/4)-S_1(2Q,R,\pi/4)-12E^0)\ . \quad (17)$$

The calculation of β_{zxx} and γ_{xxzz} is not straightforward as it requires the previous knowledge of the other components of the respective tensors.

$A_{z,zz}$ and $A_{x,zx}$ are obtained from (2) and (5) as follows:

$$A_{z,zz}=-(R^5/4Q^2)S_3(Q,R,0)\ , \quad (18)$$

$$A_{z,zz}+4A_{x,zx}=-(2^{1/2}R^5/Q^2)S_3(Q,R,\pi/4)\ . \quad (19)$$

Last, from (2) and (6) we obtain three of the four independent components of $B_{\alpha\beta,\gamma\delta}$ as

$$B_{zz,zz}=(R^7/12Q^3)(2S_4(Q,R,0)-S_4(2Q,R,0))\ , \quad (20)$$

$$B_{xx,xx}=(R^7/12Q^3)(2S_4(Q,R,\pi/2)-S_4(2Q,R,\pi/2))\ , \quad (21)$$

$$\tfrac{1}{2}B_{zz,zz}+B_{xx,xx}+4B_{xz,xz}+B_{xx,zz} = (R^7/12Q^3)(2S_4(Q,R,\pi/4)-S_4(2Q,R,\pi/4)). \quad (22)$$

From (20), (21) and (22) we calculate the value of the isotropic component $\bar{B}$, defined as [15]

$$\bar{B}=(2/15)(B_{zz,zz}+4B_{xz,xz}+B_{xx,zz}+4B_{xx,xx}) \ . \quad (23)$$

The independent components of $C_{\alpha\beta,\gamma\delta}$ and $E_{\alpha,\beta\gamma\delta}$ are calculated from the induced quadrupole and octopole moments as in previous work [11]. SCF values only are reported for the aforementioned polarizabilities in this work.

SCF and correlated values for all the independent components of μ_α, $\Theta_{\alpha\beta}$, $\Omega_{\alpha\beta\gamma}$, $\Phi_{\alpha\beta\gamma\delta}$, $\alpha_{\alpha\beta}$, $\beta_{\alpha\beta\gamma}$, $\gamma_{\alpha\beta\gamma\delta}$, $A_{\alpha,\beta\gamma}$ and three of the four independent ones of $B_{\alpha\beta,\gamma\delta}$ were calculated using (7)–(22). Electron correlation effects were taken into account via Møller-Plesset Perturbation Theory (MPPT). We refer to Krishnan and Pople [17], Hubač and Čársky [18] and Kutzelnigg [19] for a presentation of MPPT and a discussion of its relative merits. A comprehensive introduction to Rayleigh-Schrödinger Many-Body Perturbation Theory may be found in standard textbooks [20]. In this work we use SDQ-MPPT (4), fourth-order Møller-Plesset PT with single, double and quadruple substitutions from the reference SCF wavefunction. Following Krishnan and Pople [17] we write the fourth-order, MPPT(4), approximation to the energy of the molecule as

$$E=E_{\mathrm{SCF}}+E^{(2)}+E^{(3)}+E_S^{(4)}+E_D^{(4)}+E_T^{(4)}+E_Q^{(4)} +E_R^{(4)} \ . \quad (24\,\mathrm{a})$$

We assume, as we may, a similar decomposition for any property P and write

$$P=P_{\mathrm{SCF}}+P^{(2)}+P^{(3)}+P_S^{(4)}+P_D^{(4)}+P_T^{(4)}+P_Q^{(4)} +P_R^{(4)} \ , \quad (24\,\mathrm{b})$$

where, in both equations, the right side terms are the SCF, second and third order contributions, the fourth order ones arising from single, double, triple and quadrupole substitutions with reference to the SCF wavefunction and the renormalization term, respectively. The various approximations to the complete fourth-order expansion of (24) are then defined as

$$\mathrm{MPPT}(2)=P_{\mathrm{SCF}}+P^{(2)} \ , \quad (25)$$

$$\mathrm{MPPT}(3)=\mathrm{MPPT}(2)+P^{(3)} \ , \quad (26)$$

$$\mathrm{DQ\text{-}MPPT}(4)=\mathrm{MPPT}(3)+P_D^{(4)}+P_Q^{(4)}+P_R^{(4)} \equiv \mathrm{MPPT}(3)+P_{DQR}^{(4)} \ , \quad (27)$$

$$\mathrm{SDQ\text{-}MPPT}(4)=\mathrm{MPPT}(3)+P_{DQR}^{(4)}+P_S^{(4)} \equiv \mathrm{MPPT}(3)+P_{SDQR}^{(4)} \ , \quad (28)$$

$$\mathrm{SDTQ\text{-}MPPT}(4)\equiv\mathrm{MPPT}(4) =\mathrm{SDQ\text{-}MPPT}(4)+P_T^{(4)} \ . \quad (29)$$

The inclusion of the triple substitutions, as in (29), increases considerably the computational cost of the calculations. The SDQ-MPPT(4) approximation is a reasonable compromise as the loss of accuracy brought about by the exclusion of the $P_T^{(4)}$ term does not make SDQ-MPPT(4) appreciably less successful than the full MPPT(4) in electrical property predictions [13, 21].

The use of N^{th}-order MBPT in calculations of atomic/molecular properties does not always guarantee the reliability of the results. In order to accept the MBPT(N) value of a given property as a reliable prediction one should have to assess how close MBPT(N) is to MBPT(∞), i.e. whether MBPT(N) $\simeq$ MBPT(∞). Several attempts have been made to study the convergence behaviour of the perturbation series [22]. Recently, Padé approximant estimates have been obtained for the limit MBPT(∞) and for various properties [23], but with variable success. There seems to be no universally applicable algorithm for this problem. In general, fourth order MPPT should be expected to yield reliable predictions of electrical properties provided that the respective limit MPPT(∞) is not far from the reference P_{SCF} value and the state of the system under consideration is not near-degenerate.

III. Results and Discussion

The choice of a suitable basis set occupies a central position in ab initio calculations of electric moments and polarizabilities. Conventional basis sets need to be suitably enlarged in order to be used in such studies. The basis set should describe equally well the system under consideration, either free or in the presence of an electric perturbation. The degreee of difficulty of a particular study depends on the 'softness' of the system and increases in the order (positive ions) < (uncharged systems) < (negative ions). Thus, if we consider the sequence Li^+, Li, Li^-, the positive ion is a particularly hard system while the atom Li is a soft and the negative ion an a extremely soft one. Their dipole polarizability is 0.1882, 169.1 and 1097 $e^2 a_0^2 E_h^{-1}$, respectively (near-Hartree-Fock results), [24]). HCO^+ and NNH^+ are isoelectronic to CO and N_2 but it is reasonable to anticipate that the magnitude of their electric polarizabilities is smaller than that of the respective neutral species. What is more, moderately sized basis sets should

Table 1. Energy and electric moments for HCO^+ calculated with basis set A[a] at the experimental geometry[b].

	E^0	μ_z^0	Θ_{zz}^0	Ω_{zzz}^0	Φ_{zzzz}^0
SCF	−112.965301	1.640	4.173	11.16	40.0
$P^{(2)}$	−0.263194	−0.267	−0.196	0.14	−0.4
$P^{(3)}$	0.007717	0.074	0.059	−0.11	−0.3
$P^{(4)}_{DQR}$	−0.007199	−0.028	−0.037	−0.04	−0.2
$P^{(4)}_{SDQR}$	−0.013552	−0.030	−0.082	−0.07	−0.2
MPPT(2)	−113.228495	1.372	3.978	11.31	39.6
MPPT(3)	−113.220778	1.447	4.035	11.20	39.3
DQ-MPPT(4)	−113.227977	1.418	3.999	11.17	39.1
SDQ-MPPT(4)	−113.234331	1.417	3.953	11.14	39.1

[a] (5s1p/10s6p1d/10s6p1d) [3s1p/5s3p1d/5s3p1d].
[b] Coordinates of the nuclei: O(0,0,−1.11242), C(0,0,0.97573) and H(0,0,3.04498). The electric moments are calculated relative to the origin (0,0,0).

Table 2. Dipole polarizabilities, first and second dipole hyperpolarizabilities for HCO^+ calculated with basis set A[a] at the experimental geometry[b].

	α_{zz}	α_{xx}	β_{zzz}	β_{zxx}	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}
SCF	13.20	6.76	−14.90	−1.33	158	88	56
$P^{(2)}$	0.28	0.18	7.41	0.58	28	9	−2
$P^{(3)}$	−0.09	−0.07	−1.47	−0.18	−15	−3	2
$P^{(4)}_{DQR}$	0.10	0.01	0.85	0.16	3	1	−2
$P^{(4)}_{SDQR}$	−0.07	0.01	0.62	0.32	53	2	−2
MPPT(2)	13.48	6.94	−7.49	−0.75	186	97	54
MPPT(3)	13.39	6.87	−8.96	−0.94	171	94	56
DQ-MPPT(4)	13.49	6.87	−8.11	−0.78	174	95	54
SDQ-MPPT(4)	13.32	6.87	−8.35	−0.62	224	97	54

[a] See footnote a, Table 1. [b] See footnote b, Table 1.

Table 3. Dipole-quadrupole and dipole-dipole-quadrupole polarizabilities for HCO^+ calculated with basis set A[a] at the experimental geometry[b].

	$A_{z,zz}$	$A_{x,zx}$	$B_{zz,zz}$	$B_{xx,xx}$	$B_{xz,xz}+\frac{1}{4}B_{xx,zz}$	$\bar{B}$[c]
SCF	9.82	3.36	−84	−30	−18	−37
$P^{(2)}$	1.71	0.23	−9	−2	−2	−3
$P^{(3)}$	−0.63	−0.12	7	0.4	1	2
$P^{(4)}_{DQR}$	0.34	−0.03	−3	−0.0	−0.1	−0.5
$P^{(4)}_{SDQR}$	0.39	−0.04	−1	−0.4	0.2	−0.3
MPPT(2)	11.53	3.60	−93	−32	−20	−40
MPPT(3)	10.90	3.47	−86	−31	−19	−38
DQ-MPPT(4)	11.25	3.45	−88	−31	−19	−39
SDQ-MPPT(4)	11.29	3.43	−87	−32	−19	−38

[a] See footnote a, Table 1. [b] See footnote b, Table 1. [c] Defined as $\bar{B} = 2/15(B_{zz,zz}+4B_{xz,xz}+B_{xx,zz}+4B_{xx,xx})$.

Table 4. Energy and electric moments for HCO^+ calculated with basis set B[a] at the experimental geometry[b].

	E^0	μ_z^0	Θ_{zz}^0	Ω_{zzz}^0
SCF	−112.969307	1.645	4.205	11.31
$P^{(2)}$	−0.266218	−0.278	−0.240	0.02
$P^{(3)}$	0.007513	0.073	0.056	−0.13
$P^{(4)}_{DQR}$	−0.007080	−0.028	−0.035	−0.02
$P^{(4)}_{SDQR}$	−0.013469	−0.030	−0.081	−0.03
MPPT(2)	−113.235525	1.368	3.965	11.32
MPPT(3)	−113.228012	1.441	4.021	11.19
DQ-MPPT(4)	−113.235093	1.413	3.986	11.17
SDQ-MPPT(4)	−113.241481	1.411	3.940	11.16

[a] (5s 2p/10s 6p 1d/10s 6p 1d) [3s 2p/5s 3p 1d/5s 3p 1d).
[b] See footnote b, Table 1.

describe sufficiently well the distortion of the electron distribution of the protonated species in the presence of an electric field. We carried out our calculations on HCO^+ with two basis sets: (5s 1p/10s 6p 1d/10s 6p 1d)[3s 1p/5s 3p 1d/5s 3p 1d] (hereafter Basis A) and (5s 2p/10s 6p 1d/10s 6p 1d)[3s 2p/5s 3p 1d/5s 3p 1d] (hereafter Basis B) built upon a (4s/9s 5p/9s 5p) [2s/4s 2p/4s 2p] substrate [25]. One diffuse s-GTO was added on H, C and O and one diffuse p-GTO on C and O. The exponents were chosen as to form a geometric progression with the two most diffuse ones of the initial basis set. In a further step one d-GTO was added on C and O with exponents property-optimized for a similar basis set on CH and OH [26]. A p-GTO with exponent 0.02 a_0^{-2} on H completed the construction of Basis A. Basis B contains an additional p-GTO on H with exponent 1.0 a_0^{-2}. For NNH^+ we used a (10s 6p 1d/10s 6p 1d/5s 1p) [5s 3p 1d/5s 3p 1d/3s 1p] basis set, similar to Basis A for HCO^+, but with the exponent of the p-GTO on H and the d-GTO on N optimized for the energy of the molecule in the presence of a distant electric charge. Their values are 0.98 and 1.08 a_0^{-2} respectively. All calculations were carried out at the experimental geometry [2, 7]. In both cases z is the molecular axis and the molecule is oriented as

Table 5. Dipole polarizabilities, first and second dipole hyperpolarizabilities for HCO^+ calculated with basis set B[a] at the experimental geometry[b].

	α_{zz}	α_{xx}	β_{zzz}	β_{zxx}	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}
SCF	13.21	6.77	−15.47	−1.38	161	89	56
$P^{(2)}$	0.33	0.17	7.39	0.63	24	10	−2
$P^{(3)}$	−0.08	−0.07	−1.53	−0.20	−17	−3	2
$P^{(4)}_{DQR}$	0.10	0.01	0.73	0.16	4	1	−2
$P^{(4)}_{SDQR}$	−0.07	0.01	0.49	0.32	53	2	−2
MPPT(2)	13.54	6.95	−8.08	−0.76	186	99	54
MPPT(3)	13.46	6.88	−9.61	−0.96	169	96	56
DQ-MPPT(4)	13.55	6.89	−8.88	−0.80	173	97	54
SDQ-MPPT(4)	13.39	6.88	−9.12	−0.64	222	98	54

[a] See footnote a, Table 4. [b] See footnote b, Table 1.

Table 6. Dipole-quadrupole and dipole-dipole-quadrupole polarizabilities for HCO^+ calculated with basis set B[a] at the experimental geometry[b].

	$A_{z,zz}$	$A_{x,zx}$	$B_{zz,zz}$	$B_{xx,xx}$	$B_{xz,xz}+\frac{1}{4}B_{xx,zz}$	$\bar{B}^{c}$
SCF	9.94	3.47	−87	−30	−19	−38
$P^{(2)}$	1.93	0.22	−9	−2	−2	−3
$P^{(3)}$	−0.58	−0.11	7	0.5	1	2
$P^{(4)}_{DQR}$	0.36	−0.02	−3	−0.0	−0.2	−1
$P^{(4)}_{SDQR}$	0.40	−0.04	−2	−0.4	0.1	−0.4
MPPT(2)	11.87	3.69	−96	−31	−21	−41
MPPT(3)	11.29	3.58	−90	−31	−20	−39
DQ-MPPT(4)	11.64	3.56	−93	−31	−20	−40
SDQ-MPPT(4)	11.68	3.54	−92	−31	−20	−40

[a] See footnote a, Table 4.
[b] See footnote b, Table 1.
[c] See footnote c, Table 3.

to have a zero nuclear dipole moment with H along the positive part of the axis. Consequently, all calculated electric moment and polarizability values, with the exception of the dipole polarizabilities α, β and γ, are relative to the origin (0, 0, 0). Explicit formulae for the dependence of the aforementioned values on the origin have been derived by McLean and Yoshimine [14]. In all correlation energy calculations the two innermost and the two highest virtual orbitals were frozen.

For our calculations on HCO^+ we used charges of ± 100, ± 200 e (Basis A) and ± 200, ± 400 e placed at a distance of $100\,a_0$ from the origin. The calculated molecular properties are given in Tables 1, 2, 3 (Basis A), 4, 5, and 6 (Basis B). In addition, SCF values for Φ^0_{zzzz} and the independent components of $C_{\alpha\beta,\gamma\delta}$ and $E_{\alpha,\beta\gamma\delta}$ are given in Table 10. The latter were calculated from the induced electric moments, as in previous work [11]. It should be noted that the effects of electron correlation for the hexadecapole moment were obtained only with Basis A, as the use of rather strong fields in the case of Basis B did not allow their calculation via (10). An immediate conclusion from Tables 1 – 6 is that the enlargement of Basis A does not improve substantially the calculated values. The dipole moment obtained with Basis A is $1.640\,ea_0$, only $0.005\,ea_0$ lower than the respective SCF value of $1.645\,ea_0$ for Basis B. The SDQ-MPPT(4) values are 1.417 and $1.411\,ea_0$ respectively. Comparing the SDQ-MPPT(4) values of the electric moments to their respective SCF ones we find that electron correlation reduces the SCF values in the case of Basis A by 13.6% for μ, 5.3% for Θ, 0.2% for Ω and 2.2% for Φ. The perturbation series converges in a satisfactory way for all electric moments. Convergence is also satisfactory in the case of the dipole polarizability. The SCF values obtained with Basis B are $\alpha_{zz} = 13.21$ and $\alpha_{xx} = 6.77\,e^2 a_0^2 E_h^{-1}$ while the corresponding SDQ-MPPT(4) values are 13.39 and $6.88\,e^2 a_0^2 E_h^{-1}$ respectively, 1.4 and 1.6% higher. The effects of electron correlation are more important for the first dipole hyperpolarizability where the second order correction reduces, in absolute terms, the *SCF* values by about 50%. The final, SDQ-MPPT(4), values are -8.35 and $-0.62\,e^3 a_0^3 E_h^{-2}$ for β_{zzz} and β_{zxx} respectively. The fourth order correction for the axial component of the second dipole hyperpolarizability is larger than either the second or the third order ones. Consequently, the SDQ-MPPT(4) value obtained for γ_{zzzz} is not reliable. The other two components of the second dipole hyperpolarizability do not conform to this pattern. In a similar situation it is perhaps more advantageous to consider the isotropic component, defined as $\bar{\gamma} = (1/15)\ (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})$ [15]. The SCF and SDQ-MPPT(4) values of $\bar{\gamma}$ for Basis B are 125 and $140\,e^4 a_0^4 E_h^{-3}$, respectively, a correlation correction of 12%. The effect is considerably less important for the isotropic than for the axial component, allowing for a more reliable estimate of the correlation correction in the case of the former. For $A_{\alpha,\beta\gamma}$ and $B_{\alpha\beta,\gamma\delta}$ the values predicted by the two basis sets (Tables 3 and 6) differ by 6% at most. The perturbation series converges in a satisfactory way for all calculated components. The component most affected by electron correlation is the axial one of the dipole-quadrupole polarizability, $A_{z,zz}$, in which case the SDQ-MPPT(4) is 15.0% (Basis A) and 17.5% (Basis B) of the SCF value. The only electrical property of HCO^+ for which theoretical values are avariable in the literature is the dipole moment. In order to compare our values to those obtained by other workers we computed this property relative to the centre of mass. Our Basis B values are, in debyes, 4.445 and 3.850 D for SCF and SDQ-MPPT(4) respectively. Woods et al. [6] obtained a SCF value of 4.3 D, close to ours. The SCF value of Haese and Woods [7] is 4.48 D while their SD-CI one is 4.07 D, the former being in better agreement with ours than the latter. Rogers and Hillman [9] obtained the SCF values of 4.717 and 4.539 D with the standard basis sets 4-31G and 6-31G**. DeFrees et al. [10] obtained 3.96 D from a SD-CI calculation with a DZP (double zeta plus polarization) basis set, only 3% higher than our SDQ-MPPT(4) value of 3.850 D.

Our values for NNH^+ are given in Tables 7, 8, 9, and 10. Charges of ± 200 and $\pm 400\,e$ at $R = 100\,a_0$ were used in all calculations for this system. As in the case of Basis B for HCO^+ we did not calculate the electron correlation effects for the hexadecapole moment. The SCF value of this property was calculated from the SCF wavefunction and is given in Table 10. The calculated values for the dipole, quadrupole and octopole moments are in Table 7. Electron correlation changes the SCF values of these properties by $+1.1$, -7.2 and

Table 7. Energy and electric moments for NNH$^+$ calculated at the experimental geometry[a, b].

	E^0	μ_z^0	Θ_{zz}^0	Ω_{zzz}^0
SCF	−109.154811	1.219	4.304	13.78
$P^{(2)}$	−0.314834	0.069	−0.327	−0.63
$P^{(3)}$	0.004074	−0.048	0.077	0.04
$P_{\mathrm{DQR}}^{(4)}$	−0.005006	0.007	−0.034	−0.09
$P_{\mathrm{SDQR}}^{(4)}$	−0.009573	−0.007	−0.040	−0.05
MPPT(2)	−109.469646	1.288	3.977	13.15
MPPT(3)	−109.465571	1.240	4.054	13.19
DQ-MPPT(4)	−109.470578	1.247	4.019	13.09
SDQ-MPPT(4)	−109.475144	1.233	4.013	13.14

[a] Basis set (10s6p1d/10s6p1d/5s1p) [5s3p1d/5s3p1d/3s1p].
[b] Coordinates of the nuclei: N(0, 0, −1.23361), N(0, 0, 0.83564) and H(0, 0, 2.78584). The electric moments are calculated relative to the origin (0, 0, 0).

−4.6% respectively. The second order term $P^{(2)}$ dominates the correlation correction in all cases. Our values for the dipole polarizability at the SCF level are 14.30 and 5.58 $e^2 a_0^2 E_h^{-1}$ for α_{zz} and α_{xx} respectively. The perturbation series converges rapidly enough for both components. Their SDQ-MPPT(4) values are 13.81 and 5.70 $e^2 a_0^2 E_h^{-1}$. Consequently, electron correlation reduces the magnitude of the anisotropy $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$ [15] by about 7%. The MPPT series does not seem to converge for either component of the first dipole hyperpolarizability. It is obvious that the SCF value of the axial component does not constitute a reliable prediction of even the sign of β_{zzz}. Although convergence at some higher level cannot be excluded, it would be instructive to calculate both components using a conventional MCSCF or CI method. The situation appears to be less problematic in the case of the second dipole hyperpolarizability. The axial component has an SCF value of 177 $e^4 a_0^4 E_h^{-3}$ while the second order correction amounts to 165 $e^4 a_0^4 E_h^{-3}$. The perturbation series converges rapidly beyond the second order, as in the case of the isoelectronic N_2 [13b]. The SCF value of $A_{z,zz}$ for NNH$^+$ is 2.40 $e^2 a_0^3 E_h^{-1}$ con-

Table 8. Dipole polarizabilities, first and second dipole hyperpolarizabilities for NNH$^+$ calculated at the experimental geometry[a, b].

	α_{zz}	α_{xx}	β_{zzz}	β_{zxx}	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}
SCF	14.30	5.58	2.40	−1.70	177	82	54
$P^{(2)}$	−0.96	0.14	−7.73	1.49	165	3	−2
$P^{(3)}$	0.38	−0.08	2.56	−0.55	−52	1	0.4
$P_{\mathrm{DQR}}^{(4)}$	−0.04	0.02	−1.34	0.28	19	−1	−0.4
$P_{\mathrm{SDQR}}^{(4)}$	0.08	0.06	0.97	0.38	25	1	−0.4
MPPT(2)	13.34	5.73	−5.33	−0.20	342	85	52
MPPT(3)	13.73	5.65	−2.77	−0.75	290	86	52
DQ-MPPT(4)	13.69	5.67	−4.10	−0.47	309	85	52
SDQ-MPPT(4)	13.81	5.70	−1.80	−0.37	315	87	52

[a] See footnote a, Table 7 for the definition of the basis set.
[b] Geometry as in footnote b, Table 7.

Table 9. Dipole-quadrupole and dipole-dipole-quadrupole polarizabilities for NNH$^+$ calculated at the experimental geometry[a, b].

	$A_{z,zz}$	$A_{x,zx}$	$B_{zz,zz}$	$B_{xx,xx}$	$B_{xz,xz} + \frac{1}{4} B_{xx,zz}$	$\bar{B}$[c]
SCF	2.40	−2.80	−91	−22	−16	−32
$P^{(2)}$	0.13	−0.71	−8	−2	−3	−4
$P^{(3)}$	0.05	0.32	3	1	1	1
$P_{\mathrm{DQR}}^{(4)}$	−0.03	−0.12	−1	−0.2	−1	−1
$P_{\mathrm{SDQR}}^{(4)}$	0.14	−0.18	−5	−1	−1	−2
MPPT(2)	2.53	−3.50	−99	−24	−19	−36
MPPT(3)	2.58	−3.18	−96	−24	−18	−35
DQ-MPPT(4)	2.55	−3.30	−97	−24	−19	−36
SDQ-MPPT(4)	2.72	−3.36	−101	−25	−19	−37

[a] Basis set as defined in footnote a, Table 7. [b] Geometry as in footnote b, Table 7.
[c] $\bar{B} = 2/15\,(B_{zz,zz} + 4B_{xz,xz} + B_{xx,zz} + 4B_{xx,xx})$.

Table 10. SCF hexadecapole moments, quadrupole and dipole-octopole polarizabilities for HCO^{+}[a] and NNH^{+}[b] calculated at the respective experimental geometries.

	HCO^+		NNH^+[e]
	Basis set A[c]	Basis set B[d]	
Φ_{zzzz}	39.875	40.369	33.365
$C_{zz,zz}$	30.88	31.13	24.16
$C_{xz,xz}$	14.17	14.51	12.36
$C_{xx,xx}$	10.87	10.93	8.12
$E_{z,zzz}$	59.5	60.2	44.0
$E_{x,xxx}$	− 16.4	− 16.9	− 13.9

[a] Geometry as in footnote b, Table 1.
[b] Geometry as in footnote b, Table 7.
[c] See footnote a, Table 1. [d] See footnote a, Table 4.
[e] Basis set as in footnote a, Table 7.

siderably less than the same value for HCO^+. The $A_{x,zx}$ components are of comparable magnitude but with opposite sign. Electron correlation changes the calculated SCF values of the dipole-quadrupole polarizability components by 9 – 19%. The final, SDQ-MPPT(4), value of the isotropic component $\bar{B}$ is $-37\,e^3 a_0^4 E_h^{-2}$, close to the value predicted for HCO^+. As in the case of the latter, we computed the dipole moment of NNH^+ relative to the centre of mass in order to compare our values to those obtained by other workers. Our values are, in debyes, 3.340 and 3.376 D at the SCF and SDQ-MPPT(4) levels respectively. Green et al. [4] calculated an SCF value of 3.4 ± 0.5 D, quite close to ours. Hillier and Kendrick [5] used a basis set similar to the one used in the present study and obtained the values of 3.35 (SCF) and 3.24 (SD-CI) D. Their values pertain to the respective theoretical geometries and are not strictly comparable to ours. The SCF and SD-CI values of Haese and Woods are 3.38 and 3.50 D respectively [7]. As in the case of HCO^+ the former agrees better with our respective value than the latter. Montgomery and Dykstra [8] reported

Table 11. Electrostatic, E_{elec}, and inductive, E_{ind}, part of the interaction energy[a] of the system e − HCO^{+}[b,c].

	$\theta = 0$	$\pi/4$	$\pi/2$	$3\pi/4$	π
$R =$ 4	− 0.50198	− 0.31534	− 0.23193	− 0.18548	− 0.20827 (electrostatic)
	− 0.05843	− 0.03027	− 0.01228	− 0.02260	− 0.04030 (inductive)
6	− 0.24573	− 0.20021	− 0.15888	− 0.13864	− 0.13693
	− 0.00846	− 0.00501	− 0.00255	− 0.00397	− 0.00602
8	− 0.16291	− 0.14425	− 0.12136	− 0.10886	− 0.10598
	− 0.00229	− 0.00146	− 0.00082	− 0.00121	− 0.00171
10	− 0.12219	− 0.11232	− 0.09805	− 0.08945	− 0.08703
	− 0.00086	− 0.00057	− 0.00034	− 0.00049	− 0.00067
12	− 0.09790	− 0.09186	− 0.08218	− 0.07589	− 0.07396
	− 0.00039	− 0.00027	− 0.00016	− 0.00023	− 0.00031
14	− 0.08172	− 0.07767	− 0.07069	− 0.06590	− 0.06435
	− 0.00020	− 0.00014	− 0.00009	− 0.00013	− 0.00017
16	− 0.07016	− 0.06726	− 0.06200	− 0.05823	− 0.05697
	− 0.00012	− 0.00008	− 0.00005	− 0.00007	− 0.00010
18	− 0.06148	− 0.05930	− 0.05520	− 0.05216	− 0.05111
	− 0.00007	− 0.00005	− 0.00003	− 0.00005	− 0.00006
20	− 0.05472	− 0.05302	− 0.04974	− 0.04723	− 0.04635
	− 0.00005	− 0.00003	− 0.00002	− 0.00003	− 0.00004
26	− 0.04116	− 0.04024	− 0.03834	− 0.03680	− 0.03625
	− 0.00002	− 0.00001	− 0.00001	− 0.00001	− 0.00001
32	− 0.03300	− 0.03242	− 0.03119	− 0.03015	− 0.02976
	− 0.00001	− 0.00000	− 0.00000	− 0.00000	− 0.00001

[a] E_{elec} is the sum of the contributions of the electric moments from zeroth through hexadecapole. E_{ind} is the sum of the contributions of the polarizabilities. The interaction energy is then $E_{\text{int}} = E_{\text{elec}} + E_{\text{ind}}$. See Eq. (1) for the exact definition of all contributions to E_{int}.
[b] The molecule is on the z axis, as in footnote b of Table 1, and the electron on the xz plane with its position defined by the polar coordinates (R, θ).
[c] SCF values (Basis B).

SCF and SCEP (Self-consistent electron pairs) calculations in good agreement with ours. Their best value was obtained with a TZP (triple zeta plus polarization) basis set and is only about 1% higher than our SDQ-MPPT(4) one. Last, DeFrees et al. [10] obtained an SD-CI value of 3.39 D with a DZP basis set. Their value is in excellent agreement with our 3.376 D, less than 0.5% higher.

The theory of electric moments and polarizabilities is of capital importance to intermolecular interaction studies [15]. An interesting application of this theory is the accurate description of the interaction of atomic or molecular systems with charged particles. The interaction energy for the system (molecule) + (charged particle) is obtained from (2). We assume that the molecule has a fixed position in space so that the interaction energy depends only on the charge and the coordinates of the particle, $E_{\text{int}} \equiv E_{\text{int}}(Q, R, \theta) = E(Q, R, \theta) - E^0$. The total interaction energy is the sum of the electrostatic terms (E_{elec}, electric moments from zeroth through hexadecapole) and the inductive terms (E_{ind}, electric polarizabilities) as defined by (1) and (2). In Tables 11 and 12 we give the interaction energy of an electron with HCO^+ and NNH^+, respectively. For each specified position of the electron E_{int} is obtained as the sum of E_{elec} (top number) and E_{ind} (bottom number). For both systems E_{elec} is the dominant term while E_{ind} becomes important as the electron comes closer to the molecule.

IV. Conclusions

We have calculated electric moments and polarizabilities for two molecular ions of astrophysical interest, HCO^+ and NNH^+. All properties were calculated from the energy and the induced electric moments of the molecular ion in the presence of a distant electric charge. Electron correlation effects were accounted for by Møller-Plesset Perturbation

Table 12. Electrostatic, E_{elec}, and inductive, E_{ind}, part of the interaction energy[a] of the system e − NNH^{+} [b,c].

	$\theta = 0$	$\pi/4$	$\pi/2$	$3\pi/4$	π
$R =$ 4	−0.47981 −0.04733	−0.29803 −0.02347	−0.22855 −0.00983	−0.20916 −0.02657	−0.22005 (electrostatic) −0.04245 (inductive)
6	−0.23539 −0.00740	−0.19200 −0.00415	−0.15830 −0.00208	−0.14782 −0.00456	−0.14643 −0.00677
8	−0.15685 −0.00211	−0.13958 −0.00126	−0.12117 −0.00067	−0.11380 −0.00136	−0.11202 −0.00196
10	−0.11822 −0.00082	−0.10933 −0.00051	−0.09797 −0.00028	−0.09256 −0.00054	−0.09107 −0.00077
12	−0.09510 −0.00038	−0.08978 −0.00024	−0.08214 −0.00013	−0.07803 −0.00025	−0.07683 −0.00036
14	−0.07964 −0.00020	−0.07613 −0.00013	−0.07067 −0.00007	−0.06746 −0.00014	−0.06648 −0.00019
16	−0.06856 −0.00012	−0.06608 −0.00008	−0.06199 −0.00004	−0.05942 −0.00008	−0.05861 −0.00011
18	−0.06021 −0.00007	−0.05837 −0.00005	−0.05519 −0.00003	−0.05309 −0.00005	−0.05242 −0.00007
20	−0.05368 −0.00005	−0.05227 −0.00003	−0.04973 −0.00002	−0.04799 −0.00003	−0.04741 −0.00005
26	−0.04054 −0.00002	−0.03979 −0.00001	−0.03834 −0.00001	−0.03725 −0.00001	−0.03687 −0.00002
32	−0.03259 −0.00001	−0.03212 −0.00000	−0.03118 −0.00000	−0.03044 −0.00000	−0.03018 −0.00001

[a] See footnote a, Table 11. [c] SCF values.

[b] The molecule is on the z axis, as in footnote b of Table 7, and the electron on the xz plane with its position defined by the polar coordinates (R, θ).

Theory. The perturbation series converges rapidly for almost all properties studied in this work. The SCF and SDQ-MPPT(4) values for the dipole moment of both systems are in good agreement with all reliable results reported previously by other authors.

Acknowledgements

The author is grateful to Professor. Georges Leroy for his generous hospitality. Thanks are also due to Drs. Michel Sana and Daniel Peeters and Mr. Charles Dogimont for useful discussions and technical assistance.

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