

The dissociation energies of $\text{NF}(X^3\Sigma^-)$ and $\text{NCl}(X^3\Sigma^-)$

Sotiris S. Xantheas and Thom H. Dunning, Jr.

Theory, Modeling and Simulation, Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, P.O. Box 999, MS K1-96 Richland, Washington 99352

Aristides Mavridis

Laboratory of Physical Chemistry, Department of Chemistry, National & Kapodistrian University of Athens, PO Box 64 004, Zografou, Athens, Greece

(Received 20 August 1996; accepted 13 November 1996)

We have computed potential energy functions for the ground states ($X^3\Sigma^-$) of NF and NCl using a series of correlation consistent basis sets ranging from double to sextuple zeta quality and including core-valence correlation effects in conjunction with coupled-cluster single and double excitations with perturbative treatment of triple excitations [CCSD(T)] and large internally contracted multireference configuration interaction (*ic*MRCI) wave functions. The best estimates for the dissociation energies (D_e 's) are 76.6 ± 1.3 kcal/mol for NF and 64.6 ± 1.3 kcal/mol for NCl, respectively. Our results suggest that previous experimental *estimates* for the dissociation energy of NCl are in error by as much as 15 kcal/mol. The calculated spectroscopic constants for NF and NCl are in good agreement with the measured constants. © 1997 American Institute of Physics. [S0021-9606(97)01707-8]

I. INTRODUCTION

Current interest in the isovalent diatomic radicals NF and NCl stems from the possibility of producing high concentrations of their excited ($a^1\Delta$) states which, in turn, can be potentially useful energy sources.¹⁻⁴ An important aspect of these apparently simple molecules is the existing uncertainty regarding their ground state ($X^3\Sigma^-$) dissociation energies.

For NF the situation is succinctly described by Montgomery *et al.*,³ where it is documented that the values reported in the literature vary by more than 10 kcal/mol. For instance, Huber and Herzberg⁵ list a value of 80.7 kcal/mol for D_0 as suggested by O'Hare and Wahl,⁶ the JANAF thermochemical tables⁷ recommend two values of 71.4 and 70.4 kcal/mol, while Du and Setser⁸ have extracted an upper limit of 83.3 kcal/mol from the absence of emission from the ($a^1\Delta$) state in reactions of F with NCO.

Early *ab initio* calculations on $\text{NF}(X^3\Sigma^-)$ by Andersen and Öhrn⁹ predicted a binding energy of 50.7 kcal/mol at the configuration interaction (CI) level with a minimal basis set. Bettendorff and Peyerimhoff¹⁰ obtained a D_0 of 68.3 kcal/mol at the multireference CI (MRDCI) level, including the multireference Davidson correction, with a double zeta plus polarization basis set. Finally, Montgomery *et al.*³ reported $D_0 = 76.1 \pm 0.9$ kcal/mol at the QCISD(T) level of theory extrapolated to the complete basis set (CBS) limit, a value identical to the one obtained using Pople's "Gaussian 2" (G2) method.¹¹ The G2 value represents a small improvement over the value of 75.7 kcal/mol obtained with the "Gaussian 1" (G1) method.¹¹

Spectroscopic constants for the ($X^3\Sigma^-$) ground state of NF have been experimentally determined by Jones and co-workers.¹²

The situation concerning the dissociation energy of $\text{NCl}(X^3\Sigma^-)$ is even more ambiguous. In an early study by

Clark and Clyne,¹³ a binding energy of 80 ± 2 kcal/mol was recommended based on thermochemical data. Clyne and co-workers^{14,15} later reported an enthalpy of formation, ΔH_f^0 , which corresponds to $D_0 \approx 76$ kcal/mol. These are, to the best of our knowledge, the only experimental results reported for the ground-state binding energy of this molecule.

Previous *ab initio* calculations on NCl underestimated the experimentally suggested binding energy by more than 15 kcal/mol. Previous estimates for the equilibrium dissociation energy, D_e , are 49.3 kcal/mol at the CASSCF level of theory by Lievin and Metz,¹⁶ 58.1 kcal/mol at the MP4(SDTQ) level of theory with a triple zeta quality basis set by Peterson and Woods,¹⁷ and 61.3 kcal/mol at the MRDCI level of theory by Bettendorff and Peyerimhoff.¹⁸ The largest *ab initio* calculation so far, is the MCSCF+1+2 (multiconfiguration self-consistent plus single and double replacements) calculations of Papakondylis *et al.*² with the correlation-consistent polarized valence triple zeta basis set which yielded $D_e = 55.9$ kcal/mol or 59.7 kcal/mol when corrected for the effect of higher excitations.

In contrast to the existing uncertainty in the experimental value of the dissociation energy, the bond length and other spectroscopic constants of $\text{NCl}(X^3\Sigma^-)$ are very accurately known experimentally from microwave spectroscopic studies by Hirota and co-workers.¹⁹

II. METHODOLOGY

The previous discussion suggests that an accurate theoretical determination of the ground-state dissociation energies of the two NX species is justified. To this end, we use an approach that provides an accurate treatment of electron correlation coupled with simultaneous expansion of the basis set towards the complete basis set limit. The former is achieved

by describing electron correlation at the level of coupled cluster theory including single and double excitations (RCCSD) with a perturbative estimation of the triple excitations [RCCSD(T)] from a restricted Hartree–Fock (RHF) reference wave function. In addition, we considered the internally contracted multireference single and double excitation configuration interaction (*ic*MRCI) method²⁰ from a full valence complete active space self-consistent field (CASSCF) wave function. Among all methods used, the CCSD(T) and *ic*MRCI+Q represent the highest level applied in the present work.

The basis set expansion uses the family of correlation consistent basis sets of double- through sextuple- ζ quality (cc-pVxZ, $x=D, T, Q, 5, 6$), respectively.^{21(a)–21(d)} We also considered the augmented correlation consistent basis sets (aug-cc-pVxZ) which contain additional diffuse functions for each symmetry present in the standard cc-pVxZ sets; the exponents of the extra functions are derived from calculations on the atomic negative ions.^{21(b),21(c)} Since the cc-pVxZ and aug-cc-pVxZ sets were derived from valence electron calculations, only the valence electrons (VE) were correlated when using these sets. Core and core-valence correlation effects are estimated using the corresponding core-valence (cc-pCVxZ) extension of the correlation consistent sets^{22(a),22(b)} and comparing the valence electron (VE) and all electron (AE) results with each other for these sets. In the (AE)/cc-pCVxZ calculations for NCl the chlorine ($1s$)² was not correlated.

The family of correlation consistent sets when used in conjunction with the methods outlined earlier has been shown to yield dissociation energies and structures that are in excellent agreement with experiment. For example, CCSD(T) calculations of the N₂ and HF bond energies^{21(d)} as well as the CH bond energies in the CH_{*n*} and C₂H_{*n*} series,^{22(c)} including both extrapolation to the CBS limit and core-valence correlation effects, yield D_e 's within a few tenths of a kcal/mol of the experimental values. The errors with the *ic*MRCI method are larger (1–2 kcal/mol), but show a nearly constant variation with bond type.

Use of the family of correlation consistent sets to extrapolate to the complete basis set (CBS) limit makes it feasible to identify the *intrinsic* errors of a particular level of theory, defined as the difference between the experimental value and the complete basis set (CBS) limit for that particular level of theory. The latter can be estimated by noting that both total energies and their differences exhibit a systematic convergence towards a limiting value as the basis set increases^{23(a)–23(d)} and that the convergence pattern is nearly exponential when considered with respect to the cardinal number x of the cc-pVxZ or the aug-cc-pVxZ series of the correlation consistent basis sets.

We computed the potential energy curves for NF($X^3\Sigma^-$) and NCl($X^3\Sigma^-$) using the energies of seven or eight internuclear separations around the minimum. A Dunham analysis^{24,25} is used to extract the equilibrium bond length (r_e), dissociation energy (D_e), harmonic frequency (ω_e), anharmonicity ($\omega_e x_e$), rotational constant (B_e), and vibrational–rotational coupling constant (α_e). The dissocia-

tion limit for the separated atoms is calculated using the supermolecule approach at the *ic*MRCI (the energy is computed at an internuclear separation of 100 a_0) and the sum of the separated atoms at the RCCSD(T) levels of theory, respectively. Basis set superposition error (BSSE) corrections were not taken into account; for the larger sets BSSE is negligible.

All calculations were performed using the MOLPRO program suite.²⁶

III. RESULTS AND DISCUSSION

The calculated spectroscopic constants for the ground state of NF at the RHF, RCCSD, RCCSD(T), CASSCF, and *ic*MRCI levels of theory with the cc-pVxZ basis sets are listed in Table I, the corresponding ones for NCl are presented in Table II. The “+Q” designation denotes the multireference analog²⁷ of the Davidson correction²⁸ that provides an estimate of higher-than-double excitations.

In agreement with previous calculations² performed with the cc-pVTZ set, we find that RHF yields a very poor estimate for D_e . The best RHF estimates for D_e are 19.2 kcal/mol for NF with the cc-pV6Z set and 13.7 kcal/mol for NCl with the cc-pV5Z set, respectively. In addition, RHF underestimates r_e for NF by 0.024 Å, but overestimates it by 0.035 Å for NCl (cf. Tables I and II). At the CASSCF level of theory, the same behavior is observed for D_e , but to a lesser extent. However, r_e is now overestimated for both species.

For NCl the effect of the internal contraction of the CI vector in the *ic*MRCI calculation is small when compared with the uncontracted MRCI/cc-pVTZ result of Papakondylis *et al.*² The internal contraction decreases D_e by 2.0 kcal/mol and ω_e by 10 cm⁻¹, while increasing r_e by 0.004 Å. The effect of the internal contraction for D_e is comparable with the one observed previously for O₂ and F₂ with the cc-pVxZ sets.^{23(c)} The internal contraction scheme does, however, result in substantial computational savings, reducing the length of the CI vector from 1 121 260 (uncontracted) to 39 920 (contracted) configuration state functions (CSFs) for the cc-pVTZ basis set (length of contracted CI vector is 3.6% of the uncontracted one). This makes calculations at this level of theory feasible with the larger sets for which the contraction is even more advantageous. For example, the ratio of the number of contracted to uncontracted CSFs is 307 248/13 039 720 (or 2.4%) for the cc-pV5Z set.

It is remarkable that the RCCSD(T)/cc-pVTZ results of $D_e = 56.0$ kcal/mol and $r_e = 1.640$ Å (cf. Table II) are within 0.1 kcal/mol and 0.003 Å of the corresponding uncontracted MRCI/cc-pVTZ values.² For all cc-pVxZ sets, the *ic*MRCI+Q results for the dissociation energy of both NF and NCl are within 0.6 kcal/mol of the corresponding RCCSD(T) values; the equilibrium bond lengths are, however, slightly longer at the *ic*MRCI+Q level of theory. A calculation at the internally contracted averaged coupled-pair functional (*ic*ACPF) level of theory²⁹ with the cc-pVTZ set yields $D_e = 55.9$ kcal/mol, $r_e = 1.6446$ Å, and $\omega_e = 794.2$ cm⁻¹, results which are almost identical to the ones at the *ic*MRCI+Q level of theory with the same basis set (cf.

TABLE I. Experimental and calculated spectroscopic constants for the ground ($X^3\Sigma^-$) state of NF with the cc-pV x Z ($x=D, T, Q, 5, 6$) basis sets.

Method	Basis set	E_e (hartrees)	D_e (kcal/mol)	r_e (Å)	ω_e (cm ⁻¹)	$\omega_e X_e$ (cm ⁻¹)	B_e (cm ⁻¹)	α_e (cm ⁻¹)
Expt.			70.4–83.3 ^a	1.3170 ^b	1141.4 ^b	9.0 ^b	1.2057 ^b	0.0149 ^b
RHF	cc-pVDZ	-153.780 515	12.7	1.2977	1238.9	8.3	1.242	0.0146
	cc-pVTZ	-153.827 505	18.3	1.2942	1259.4	7.5	1.249	0.0133
	cc-pVQZ	-153.839 274	18.9	1.2934	1254.6	7.5	1.250	0.0133
	cc-pV5Z	-153.842 465	19.1	1.2932	1254.5	7.5	1.250	0.0133
	cc-pV6Z	-153.842 841	19.2	1.2931	1254.5	7.5	1.251	0.0133
RCCSD	cc-pVDZ	-154.096 797	58.0	1.3226	1149.9	9.3	1.196	0.0155
	cc-pVTZ	-154.234 320	66.4	1.3127	1186.7	8.2	1.213	0.0141
	cc-pVQZ	-154.277 041	69.2	1.3094	1186.9	8.1	1.220	0.0141
	cc-pV5Z	-154.291 629	70.3	1.3086	1187.2	8.2	1.221	0.0141
	cc-pV6Z	-154.296 613	70.8	1.3082	1188.0	8.2	1.222	0.0141
RCCSD(T)	cc-pVDZ	-154.103 930	61.6	1.3289	1121.2	9.7	1.184	0.0159
	cc-pVTZ	-154.248 306	71.4	1.3201	1155.3	8.5	1.200	0.0144
	cc-pVQZ	-154.293 085	74.5	1.3174	1153.1	8.5	1.205	0.0145
	cc-pV5Z	-154.308 491	75.7	1.3169	1152.2	8.6	1.206	0.0146
	cc-pV6Z	-154.313 766	76.2	1.3165	1152.7	8.6	1.206	0.0145
CASSCF	cc-pVDZ	-153.835 837	47.4	1.3338	1076.6	11.7	1.175	0.0178
	cc-pVTZ	-153.881 475	52.2	1.3260	1117.3	10.6	1.189	0.0161
	cc-pVQZ	-153.893 071	52.7	1.3248	1115.8	10.6	1.192	0.0161
	cc-pV5Z	-153.896 167	52.8	1.3244	1116.2	10.6	1.192	0.0161
	cc-pV6Z	-153.896 521	52.9	1.3243	1116.3	10.6	1.192	0.0161
<i>ic</i> MRCI	cc-pVDZ	-154.090 971	60.8	1.3319	1104.5	10.3	1.179	0.0165
	cc-pVTZ	-154.223 058	69.4	1.3211	1148.6	9.2	1.198	0.0149
	cc-pVQZ	-154.263 757	72.1	1.3176	1150.9	9.1	1.205	0.0149
	cc-pV5Z	-154.277 685	73.1	1.3166	1152.2	9.1	1.206	0.0150
	cc-pV6Z	-154.282 449	73.5	1.3162	1153.3	9.1	1.207	0.0150
<i>ic</i> MRCI+Q	cc-pVDZ	-154.105 788	62.0	1.3336	1101.6	10.1	1.176	0.0164
	cc-pVTZ	-154.246 098	71.1	1.3240	1141.7	8.9	1.193	0.0147
	cc-pVQZ	-154.289 448	74.0	1.3209	1142.2	8.9	1.199	0.0148
	cc-pV5Z	-154.304 206	75.1	1.3202	1142.5	8.9	1.200	0.0148
	cc-pV6Z	-154.309 241	75.6	1.3197	1143.3	8.9	1.201	0.0148

^aReferences 5–8.^bReference 12.

Table II). The previous discussion suggests that out of all methods initially considered, only RCCSD(T) and *ic*MRCI yield accurate energetics (especially when the “+Q” correction is applied), with the RCCSD(T) method also providing more accurate r_e 's and ω_e 's.

The effect of diffuse functions in the basis set was investigated by computing the spectroscopic constants and dissociation energies at the RCCSD(T) and *ic*MRCI levels of theory with the family of aug-cc-pV x Z ($x=D, T, Q, 5$) sets. The results, shown in Table III, suggest that the dissociation energies for both species converge “faster” with basis set size for the aug-cc-pV x Z sets. The net effect of augmentation, however, decreases as the basis set increases—for the 5Z set the effect on D_e is of the order of 0.5 kcal/mol for both species. For NF, the magnitude of D_e with the aug-cc-pV5Z and cc-pV6Z sets are within 0.1 kcal/mol. In addition, the aug-cc-pV x Z sets produce longer equilibrium bond lengths for NF, but shorter ones for NCl, partially correcting for the fact that the plain sets underestimate r_e for NF, but overestimate it for NCl.

Finally, we have estimated core-valence correlation effects using the cc-pCV x Z sets ($x=D, T, Q$) at the RCCSD(T) level of theory. The results are shown in Table IV. In this table the notation VE indicates that only the va-

lence electrons were correlated as opposed to AE which denotes correlation of all electrons. Since the cc-pCV x Z sets are larger than the cc-pV x Z sets, they produce slightly different results when only the valence electrons are correlated. This difference, however, diminishes as the basis set size increases (cf. Tables I, II, and IV).

Figure 1 traces the dependence of the dissociation energy of NF on the size of the basis set for the correlation consistent sets considered in this study. The analogous results for NCl are shown in Fig. 2. Previous results on various first/second row mixed diatomics,^{23(a)–23(d),30} triatomics³¹ as well as a variety of intermolecular complexes^{32–34} have suggested a systematic convergence of properties such as dissociation energies and equilibrium bond lengths with basis set size within a given level of theory. To model this behavior, a *heuristic* approach has been used,^{23,30,31–34} that assumes a functional dependence of a specific property with basis set size that is used to extrapolate to the CBS limit by a least means squares fitting. A commonly used function is the exponential

$$P_n = P_{\text{CBS}} + c \exp(-d \cdot n), \quad (1)$$

where n is the cardinal number of the basis set (2–6 for double through sextuple) and c, d are adjustable constants.

TABLE II. Experimental and calculated spectroscopic constants for the ground ($X^3\Sigma^-$) state of NCl with the cc-pVxZ ($x=D,T,Q,5$) basis sets.

Method	Basis set	E_e (hartrees)	D_e (kcal/mol)	r_e (Å)	ω_e (cm^{-1})	$\omega_e X_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})
Expt.			76-(80±2) ^a	1.6107 ^b	828.0 ^b	5.3 ^b	0.650 ^b	0.0064 ^b
RHF	cc-pVDZ	-513.865 577	6.3	1.6767	812.2	3.7	0.600	0.0049
	cc-pVTZ	-513.896 254	12.0	1.6555	830.0	3.5	0.615	0.0046
	cc-pVQZ	-513.904 143	13.0	1.6493	832.2	3.6	0.620	0.0046
	cc-pV5Z	-513.906 490	13.7	1.6453	833.3	3.6	0.623	0.0046
RCCSD	cc-pVDZ	-514.141 747	41.7	1.6739	782.8	5.3	0.602	0.0061
	cc-pVTZ	-514.259 168	51.1	1.6367	819.6	4.7	0.629	0.0058
	cc-pVQZ	-514.294 738	55.0	1.6225	832.6	4.7	0.640	0.0059
	cc-pV5Z	-514.307 066	57.1	1.6141	838.5	4.7	0.647	0.0059
RCCSD(T)	cc-pVDZ	-514.149 471	45.4	1.6783	768.5	5.7	0.599	0.0063
	cc-pVTZ	-514.275 175	56.0	1.6399	807.0	5.0	0.627	0.0061
	cc-pVQZ	-514.313 483	60.3	1.6253	820.4	5.1	0.638	0.0062
	cc-pV5Z	-514.326 839	62.6	1.6164	827.2	5.1	0.645	0.0063
CASSCF	cc-pVDZ	-513.909 570	33.9	1.7147	690.8	6.6	0.573	0.0070
	cc-pVTZ	-513.939 203	38.9	1.6864	722.7	5.9	0.593	0.0064
	cc-pVQZ	-513.946 808	39.8	1.6786	726.8	5.9	0.598	0.0065
	cc-pV5Z	-513.948 959	40.4	1.6737	729.4	5.9	0.602	0.0064
<i>ic</i> MRCI	cc-pVDZ	-514.134 082	44.4	1.6863	746.4	6.2	0.593	0.0066
	cc-pVTZ	-514.243 267	53.9	1.6472	788.1	5.4	0.621	0.0063
	cc-pVQZ	-514.276 192	57.5	1.6329	801.7	5.4	0.632	0.0063
<i>ic</i> MRCI+Q	cc-pV5Z	-514.287 594	59.5	1.6245	808.0	5.3	0.639	0.0063
	cc-pVDZ	-514.151 978	45.8	1.6842	751.8	6.2	0.594	0.0066
	cc-pVTZ	-514.273 297	55.9	1.6447	793.9	5.4	0.623	0.0063
	cc-pVQZ	-514.309 773	60.0	1.6297	808.7	5.3	0.635	0.0063
	cc-pV5Z	-514.322 306	62.2	1.6208	815.8	5.3	0.642	0.0063

^aReferences 13–15.^bReference 19.TABLE III. Calculated spectroscopic constants for the ground ($X^3\Sigma^-$) state of NF and NCl with the aug-cc-pVxZ ($x=D,T,Q,5$) basis sets for RCCSD(T), *ic*MRCI, and *ic*MRCI+Q.

Method	Basis set	E_e (hartrees)	D_e (kcal/mol)	r_e (Å)	ω_e (cm^{-1})	$\omega_e X_e$ (cm^{-1})	B_e (cm^{-1})	α_e (cm^{-1})
NF								
RCCSD(T)	aug-cc-pVDZ	-154.141 167	65.6	1.3446	1079.8	7.9	1.157	0.0143
	aug-cc-pVTZ	-154.260 373	73.0	1.3246	1131.3	8.3	1.192	0.0145
	aug-cc-pVQZ	-154.297 865	75.4	1.3189	1145.5	8.5	1.202	0.0146
	aug-cc-pV5Z	-154.310 417	76.1	1.3174	1149.7	8.5	1.205	0.0146
<i>ic</i> MRCI	aug-cc-pVDZ	-154.122 735	64.6	1.3446	1075.6	8.4	1.157	0.0148
	aug-cc-pVTZ	-154.232 742	70.8	1.3241	1131.5	8.9	1.193	0.0149
	aug-cc-pVQZ	-154.267 633	72.9	1.3185	1146.3	9.1	1.203	0.0150
	aug-cc-pV5Z	-154.279 285	73.4	1.3170	1150.8	9.1	1.206	0.0150
<i>ic</i> MRCI+Q	aug-cc-pVDZ	-154.141 735	65.9	1.3489	1064.3	8.2	1.149	0.0147
	aug-cc-pVTZ	-154.257 332	72.6	1.3280	1120.7	8.6	1.186	0.0148
	aug-cc-pVQZ	-154.293 865	74.8	1.3221	1136.0	8.8	1.196	0.0148
	aug-cc-pV5Z	-154.305 981	75.4	1.3206	1140.5	8.9	1.199	0.0148
NCl								
RCCSD(T)	aug-cc-pVDZ	-514.177 594	49.4	1.6741	773.8	5.3	0.602	0.0061
	aug-cc-pVTZ	-514.285 048	58.1	1.6365	807.0	5.0	0.629	0.0062
	aug-cc-pVQZ	-514.317 383	61.4	1.6238	821.6	5.1	0.639	0.0062
	aug-cc-pV5Z	-514.328 755	63.1	1.6158	827.1	5.1	0.646	0.0063
<i>ic</i> MRCI	aug-cc-pVDZ	-514.156 613	48.0	1.6810	755.4	5.9	0.597	0.0064
	aug-cc-pVTZ	-514.250 699	55.6	1.6440	789.2	5.4	0.624	0.0063
	aug-cc-pVQZ	-514.279 221	58.4	1.6317	803.1	5.4	0.633	0.0063
	aug-cc-pV5Z	-514.289 103	59.9	1.6240	808.1	5.3	0.639	0.0063
<i>ic</i> MRCI+Q	aug-cc-pVDZ	-514.178 921	49.6	1.6797	758.7	5.8	0.598	0.0064
	aug-cc-pVTZ	-514.282 320	57.9	1.6411	795.2	5.3	0.626	0.0063
	aug-cc-pVQZ	-514.313 325	61.1	1.6283	810.2	5.3	0.636	0.0063
	aug-cc-pV5Z	-514.324 027	62.7	1.6202	816.0	5.3	0.642	0.0064

TABLE IV. Calculated spectroscopic constants for the ground ($X^3\Sigma^-$) state of NF and NCl with the cc-pCV x Z ($x=D,T,Q,5$) sets for RCCSD(T).

Method	Basis set	E_e (hartrees)	D_e (kcal/mol)	r_e (Å)	ω_e (cm $^{-1}$)	$\omega_e\chi_e$ (cm $^{-1}$)	B_e (cm $^{-1}$)	α_e (cm $^{-1}$)
NF								
VE	cc-pCVDZ	-154.109 802	61.7	1.3286	1121.1	9.6	1.185	0.0159
	cc-pCVTZ	-154.255 844	71.6	1.3199	1153.6	8.4	1.200	0.0143
	cc-pCVQZ	-154.296 592	74.5	1.3170	1154.1	8.6	1.206	0.0146
	cc-pCV5Z	-154.309 976	75.7	1.3167	1152.3	8.6	1.206	0.0146
AE	cc-pCVDZ	-154.185 426	61.9	1.3278	1122.2	9.7	1.186	0.0160
	cc-pCVTZ	-154.363 086	71.7	1.3179	1156.6	8.4	1.204	0.0144
	cc-pCVQZ	-154.414 878	74.6	1.3148	1157.5	8.6	1.209	0.0146
	cc-pCV5Z	-154.431 538	75.8	1.3144	1155.9	8.6	1.211	0.0147
NCl								
VE	cc-pCVDZ	-514.155 347	46.0	1.6744	771.7	5.7	0.601	0.0063
	cc-pCVTZ	-514.282 774	57.4	1.6294	811.3	5.3	0.635	0.0062
	cc-pCVQZ	-514.318 244	61.2	1.6179	823.9	5.6	0.644	0.0063
AE	cc-pCVDZ	-514.396 067	46.3	1.6727	774.5	5.8	0.603	0.0064
	cc-pCVTZ	-514.635 029	57.6	1.6263	814.2	5.3	0.637	0.0063
	cc-pCVQZ	-514.710 651	61.5	1.6141	827.1	5.4	0.647	0.0063

The extrapolated CBS dissociation energies for NF and NCl at the RCCSD(T) level of theory are listed in Table V. Two schemes, employing extrapolation of absolute energies, and energy differences, were used. For NF, both schemes produce CBS limits that are very similar (within 0.1 kcal/mol), the second one having, however, a smaller χ^2 . Core-valence correlation effects are negligible for NF since they amount to only ~ 0.1 kcal/mol. The extrapolation scheme produces a CBS limit for the cc-pV x Z sets that is only 0.1 kcal/mol larger than the RCCSD(T)/cc-pV6Z value for the dissociation energy. The CBS limits for the cc-pV x Z aug-cc-pV x Z, and cc-pCV x Z/VE sets are within 0.4 kcal/mol of each other, the range being identical to that spanned by the values for the quintuple zeta sets. The corresponding CBS limits for the dissociation energy of NF with the cc-pV x Z (aug-cc-pV x Z) sets are 73.6 (73.7) kcal/mol at the *ic*MRCI and 75.7 (75.8) kcal/mol at the *ic*MRCI+Q levels of theory.

The variation of r_e for NF with basis set size at the RCCSD(T) level of theory is graphically shown in Fig. 3. The corresponding CBS extrapolated equilibrium bond

lengths for NF at the RCCSD(T) level of theory are shown in Table VI. The CBS limits for the cc-pV x Z, aug-cc-pV x Z, and cc-pCV x Z/VE sets all agree to within 0.0005 Å and are within 0.0008 Å of the experimental result.¹² Inclusion of core-valence correlation yields an r_e that is 0.003 Å smaller than the experimental value. This can be considered as the *intrinsic* error of the RCCSD(T) method for NF as regards prediction of equilibrium bond lengths. As for the case of the dissociation energy, the extrapolation scheme produces limits that are very close (within ~ 0.0004 Å) of the corresponding r_e 's computed with the largest basis set.

The dependence of the RCCSD(T) dissociation energy of NCl with the various basis set is shown in Fig. 2. The predicted CBS limits for D_e with the cc-pV x Z and aug-cc-pV x Z sets are both 64.1 kcal/mol, which is 1.5 and 1.0 kcal/mol larger than that obtained with the cc-pV5Z and aug-cc-pV5Z sets, respectively. The corresponding CBS limits at the *ic*MRCI and *ic*MRCI+Q levels of theory are 60.5 (60.6) kcal/mol and 63.5 (63.5) with the cc-pV x Z (aug-cc-pV x Z) sets, respectively. Again we note that extrapolating D_e 's pro-

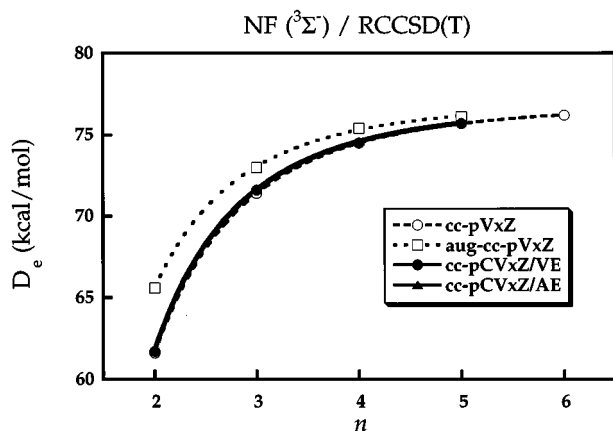


FIG. 1. Variation of the dissociation energy (D_e) of NF with basis set size at the RCCSD(T) level of theory. Lines trace an exponential fit to the data.

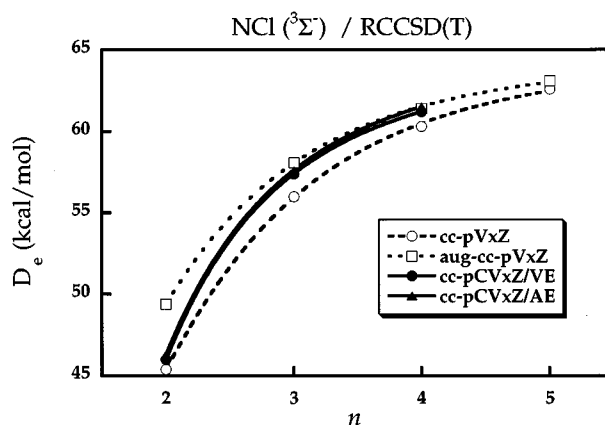


FIG. 2. Variation of the dissociation energy (D_e) of NCl with basis set size at the RCCSD(T) level of theory. Lines trace an exponential fit to the data.

TABLE V. Extrapolated CBS dissociation energies (D_e) for the ground ($X^3\Sigma^-$) state of NF and NCl at the RCCSD(T) level of theory.

Basis set	Extrapolating ΔE 's	Extrapolating total energies
NF		
cc-pVxZ	76.3±0.1	76.3±0.4
aug-cc-pVxZ	76.5±0.05	76.5±0.4
cc-pCVxZ/VE	76.1±0.2	76.1±0.6
cc-pCVxZ/AE	76.2±0.2	76.1±0.6
NCl		
cc-pVxZ	64.1±0.5 ^a	63.5±0.6 ^a
	63.2 ^b	62.8 ^b
aug-cc-pVxZ	64.1±0.3 ^a	63.8±0.6 ^a
	63.4 ^b	63.2 ^b
cc-pCVxZ/VE	63.1 ^b	63.1 ^b
cc-pCVxZ/AE	63.6 ^b	63.4 ^b

^aFour-point fit.^bThree-point fit.

duces a better fit than when extrapolating total energies and computing D_e as the difference of the corresponding CBS limits (cf. Table V). Figure 4 traces the variation of r_e with basis set.

For NCl, core-valence effects are larger than for NF, amounting to ~ 0.5 kcal/mol and 0.004 Å (cf. Tables V and VI) at the RCCSD(T) level of theory. The valence sets produce equilibrium bond lengths that are between 0.002 and 0.003 Å longer than experiment, whereas the effect of core-valence correlation results in underestimating r_e by 0.001 Å with respect to experiment [*intrinsic* error of RCCSD(T) for NCl]. The “slow convergence” of r_e with the cc-pVxZ sets can be attributed to the lack of the tight functions that are present in the cc-pCVxZ sets. For example, by comparing the RCCSD(T) results with the different variations of the quadruple zeta quality set (Tables II, III, and IV) we note that whereas the diffuse functions contribute 0.0015 Å to r_e (difference between the cc-pVQZ and aug-cc-pVQZ results), the effect of the tight functions is 0.0074 Å (difference between the cc-pVQZ and cc-pCVQZ/VE results). This effect

TABLE VI. Extrapolated CBS equilibrium bond lengths (r_e) for the ground ($X^3\Sigma^-$) state of NF and NCl at the RCCSD(T) level of theory.

Basis set	r_e (Å)
NF	
cc-pVxZ	1.3165±0.0001
aug-cc-pVxZ	1.3167±0.0001
cc-pCVxZ/VE	1.3162±0.0004
cc-pCVxZ/AE	1.3140±0.0003
Expt.	1.3170
NCl	
cc-pVxZ	1.612±0.003
aug-cc-pVxZ	1.613±0.003
cc-pCVxZ/VE	1.614 ^a
cc-pCVxZ/AE	1.610 ^a
Expt.	1.6107

^aThree-point fit.

is less pronounced for D_e where the diffuse functions make a more significant contribution (1.1 vs 0.9 kcal/mol).

Finally the effect of the exponential extrapolation with basis set size in NCl is larger than that for NF. The extrapolation amounts to ~ 0.004 Å for r_e and ~ 2 kcal/mol for D_e when compared to the corresponding numbers computed with the largest basis sets.

IV. CONCLUSIONS

Accurate calculations on the ground states ($X^3\Sigma^-$) of NF and NCl predict D_e 's of 76.6 ± 1.3 and 64.6 ± 1.3 kcal/mol, respectively. These values were obtained by extrapolating RCCSD(T) calculations with the cc-pVxZ and aug-cc-pVxZ basis sets to the complete basis set limit (76.5 kcal/mol for NF, 64.1 kcal/mol for NCl) and then including core-valence correlation effects (0.1 kcal/mol for NF, 0.5 kcal/mol for NCl). The assigned error bars are due to the extrapolation process, the choice of the functional form used in the process [Eq. (1)] and the expected *intrinsic* error of the RCCSD(T) method for similar molecules. For the isoelectronic systems O_2 and SO the *ic*MRCI+Q CBS limits are within 0.5 and 1.4 ± 1 kcal/mol^{23(c),23(d)} of the corresponding experimental

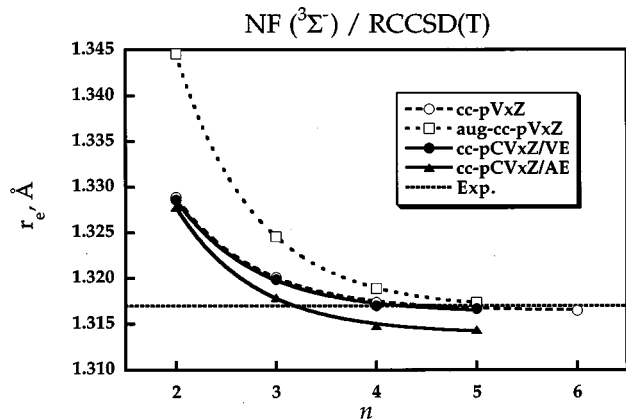


FIG. 3. Variation of the equilibrium bond length energy (r_e) of NF with basis set size at the RCCSD(T) level of theory. Lines trace an exponential fit to the data.

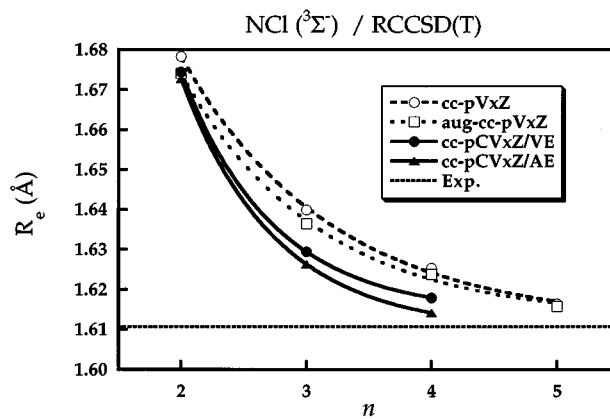


FIG. 4. Variation of the equilibrium bond length energy (r_e) of NCl with basis set size at the RCCSD(T) level of theory. Lines trace an exponential fit to the data.

values; however, for SO the experimental value is uncertain by ± 1 kcal/mol. Based on the agreement between *icMRCI+Q* and *RCCSD(T)* we expect our predicted dissociation energies to be within 1 kcal/mol of the exact values.

The present value of $D_e(\text{NF})$ agrees well with the corresponding *G2* value of 76.1 kcal/mol¹¹ as well as with the calculations of Montgomery *et al.*³ Our result for $D_e(\text{NCl})$, on the other hand, is significantly higher (3–5 kcal/mol) than obtained in previous calculations. Experimental estimates of the dissociation energies range from 70 to less than 83 kcal/mol for NF^{5-8} and from 78 to 80 kcal/mol for NCl .¹³⁻¹⁵ Our calculations narrow the range of acceptable D_e 's for NF and suggest that the previous values used for the dissociation energy of NCl are too high by as much as 15 kcal/mol.

Spectroscopic constants predicted by the *RCCSD(T)* calculations for NF yield values in good agreement with experiment: The best results with the valence sets are $r_e = 1.3165 \text{ \AA}$ (cc-pV6Z) vs 1.3170 \AA (expt.); $\omega_e = 1152.7 \text{ cm}^{-1}$ (cc-pV6Z) vs 1141.4 cm^{-1} (expt.); and $\omega_e x_e = 8.6 \text{ cm}^{-1}$ vs 8.99 cm^{-1} (expt.). Core-valence correlation effects amount to 0.0023 \AA in the bond lengths for the cc-pCV5Z set resulting in a slight underestimation of r_e with respect to experiment [the *intrinsic* error of *RCCSD(T)*]. The best results for the spectroscopic constants with the core-valence sets (cc-pCV5Z/AE results) are $r_e = 1.3144 \text{ \AA}$, $\omega_e = 1155.97 \text{ cm}^{-1}$, and $\omega_e x_e = 8.6 \text{ cm}^{-1}$. The agreement is also satisfactory of NCl; for example, the best results with the valence sets (aug-cc-pV5Z) are: $r_e = 1.6158 \text{ \AA}$, $\omega_e = 827.1 \text{ cm}^{-1}$, and $\omega_e x_e = 5.1 \text{ cm}^{-1}$. Core-valence effects are larger, amounting to 0.0038 \AA with the cc-pCVQZ set. The best results with the core-valence sets (cc-pVQZ/AE results) are $r_e = 1.6141 \text{ \AA}$ vs 1.6107 \AA (expt.), $\omega_e = 827.1 \text{ cm}^{-1}$ vs 828.0 cm^{-1} (expt.) and $\omega_e x_e = 5.4 \text{ cm}^{-1}$ vs 5.3 cm^{-1} (expt.). The *intrinsic* error of *CCSD(T)* in estimating r_e seems larger for NF than for NCl (cf. Figs. 3 and 4).

ACKNOWLEDGMENTS

We wish to thank Professor K. A. Peterson for many helpful discussions, for providing the chlorine atom core-valence sets prior to publication as well as for prepublication review of the manuscript. This work was performed under the auspices of the Division of Chemical Sciences, Office of Basic Energy Sciences, U.S. Department of Energy under Contract DE-AC06-76RLO 1830 with Battelle Memorial Institute, which operates the Pacific Northwest National Laboratory. Computer resources were provided by the Division of Chemical Sciences and by the Mathematical, Information and Computational Sciences Division, Office of Energy Research, at the National Energy Research Supercomputer Center (Berkeley, CA).

¹A. Papakondylis and A. Mavridis, *Chem. Phys. Lett.* **216**, 167 (1993).

²A. Papakondylis, A. Mavridis, and A. Metropoulos, *J. Phys. Chem.* **99**, 10759 (1995), and references therein.

³J. A. Montgomery Jr., G. A. Petersson, M. A. Al-Laham, and J. Mantzaris, *Chem. Phys. Lett.* **169**, 497 (1990).

- ⁴E. Arunan, C. P. Liu, D. W. Setser, J. W. Gilbert, and R. D. Coombe, *J. Phys. Chem.* **98**, 494 (1994).
- ⁵K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure: IV. Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ⁶P. A. G. O'Hare and A. C. Wahl, *J. Chem. Phys.* **54**, 4563 (1971); P. A. G. O'Hare, *ibid.* **59**, 3842 (1973).
- ⁷M. W. Chase Jr., C. A. Davies, J. R. Downey Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *J. Phys. Chem. Ref. Data* **11**, Suppl. 1 (1985).
- ⁸K.-Y. Du and D. W. Setser, *Chem. Phys. Lett.* **153**, 393 (1988).
- ⁹A. Andersen and Y. Ohn, *J. Mol. Spectrosc.* **45**, 358 (1973).
- ¹⁰M. Bettendorf and S. D. Peyerimhoff, *Chem. Phys.* **99**, 55 (1985).
- ¹¹J. A. Pople, M. Head-Gordon, D. J. Fox, K. Raghavachari, and L. A. Curtiss, *J. Chem. Phys.* **90**, 5622 (1989); L. A. Curtiss, K. Raghavachari, G. W. Trucks, and J. A. Pople, *ibid.* **94**, 7221 (1991).
- ¹²A. E. Douglas and W. E. Jones, *Can. J. Phys.* **44**, 2251 (1966); W. E. Jones, *ibid.* **45**, 21 (1967).
- ¹³T. C. Clark and M. A. A. Clyne, *Trans. Faraday Soc.* **66**, 877 (1970).
- ¹⁴M. A. A. Clyne and A. J. MacRobert, *J. Chem. Soc. Faraday Trans. 2* **79**, 283 (1983).
- ¹⁵M. A. A. Clyne, A. J. MacRobert, and L. J. Stief, *J. Chem. Soc. Faraday Trans. 2* **81**, 159 (1985).
- ¹⁶J. Lievin and J.-Y. Metz, *Theor. Chim. Acta* **67**, 391 (1985).
- ¹⁷K. A. Peterson and R. C. Woods, *J. Chem. Phys.* **93**, 1876 (1990).
- ¹⁸M. Bettendorf and S. D. Peyerimhoff, *Chem. Phys.* **104**, 29 (1986).
- ¹⁹C. Yamada, Y. Endo, and E. Hirota, *J. Chem. Phys.* **79**, 4159 (1983); C. Yamada, Y. Endo, and E. Hirota, *J. Mol. Spectrosc.* **117**, 105 (1986); **117**, 134 (1986).
- ²⁰H.-J. Werner and P. J. Knowles, *J. Chem. Phys.* **89**, 5803 (1988); P. J. Knowles and H.-J. Werner, *Chem. Phys. Lett.* **145**, 514 (1988); H.-J. Werner and E. A. Reinsch, *J. Chem. Phys.* **76**, 3144 (1982); H.-J. Werner, *Adv. Chem. Phys.* **LXIX**, 1 (1987).
- ²¹(a) T. H. Dunning, Jr., *J. Chem. Phys.* **90**, 1007 (1989); (b) R. A. Kendall, T. H. Dunning, Jr., and R. J. Harrison, *ibid.* **96**, 6796 (1992); (c) D. E. Woon and T. H. Dunning, Jr., *ibid.* **98**, 1358 (1993); (d) A. K. Wilson, T. van Mourik, and T. H. Dunning, Jr., *Theochem.* (in press).
- ²²(a) D. E. Woon and T. H. Dunning, Jr., *J. Chem. Phys.* **103**, 4572 (1995); (b) K. A. Peterson and T. H. Dunning, Jr. (in preparation); (c) *J. Chem. Phys.* (in press).
- ²³(a) K. A. Peterson, R. A. Kendall, and T. H. Dunning, Jr., *J. Chem. Phys.* **99**, 1930 (1993); (b) D. E. Woon and T. H. Dunning, Jr., *ibid.* **99**, 1914 (1993); (c) K. A. Peterson, R. A. Kendall and T. H. Dunning, Jr., *ibid.* **99**, 9790 (1993); (d) D. E. Woon and T. H. Dunning, Jr., *ibid.* **101**, 8877 (1994).
- ²⁴J. L. Dunham, *Phys. Rev.* **41**, 713 (1932).
- ²⁵The fitting was performed using a program written by K. A. Peterson.
- ²⁶MOLPRO is a package of *ab initio* programs written by H.-J. Werner and P. J. Knowles, with contributions from J. Almlöf, R. D. Amos, M. J. O. Deegan, S. T. Elbert, C. Hampel, W. Meyer, K. Peterson, R. Pitzer, A. J. Stone, P. R. Taylor, R. Lindh, M. E. Mura, and T. Thorsteinsson. For the *RCCSD(T)* implementation in MOLPRO see P. J. Knowles, C. Hampel and H.-J. Werner, *J. Chem. Phys.* **99**, 5219 (1993).
- ²⁷M. R. A. Blomberg and P. E. M. Siegbahn, *J. Chem. Phys.* **78**, 5682 (1983).
- ²⁸S. R. Langhoff and E. R. Davidson, *Int. J. Quantum Chem.* **8**, 61 (1974).
- ²⁹R. J. Gdanitz and R. Ahlrichs, *Chem. Phys. Lett.* **143**, 413 (1988); R. J. Cave and E. R. Davidson, *J. Chem. Phys.* **89**, 6798 (1988); P. G. Szalay and R. J. Bartlett, *Chem. Phys. Lett.* **214**, 481 (1993); H.-J. Werner and P. J. Knowles, *Theor. Chim. Acta* **78**, 175 (1990).
- ³⁰D. E. Woon, *Chem. Phys. Lett.* **204**, 29 (1993); *J. Chem. Phys.* **100**, 2838 (1994); K. A. Peterson, *ibid.* **102**, 262 (1995).
- ³¹S. S. Xantheas and T. H. Dunning, Jr., *J. Phys. Chem.* **97**, 18, 6616 (1993).
- ³²D. Feller, *J. Chem. Phys.* **96**, 6104 (1992); D. Feller, E. D. Glendening, R. A. Kendall, and K. A. Peterson, *ibid.* **100**, 4981 (1994); M. W. Feyereisen, D. Feller, and D. A. Dixon, *J. Phys. Chem.* **100**, 2993 (1996).
- ³³K. A. Peterson and T. H. Dunning, Jr., *J. Chem. Phys.* **102**, 2032 (1995).
- ³⁴S. S. Xantheas, *J. Chem. Phys.* **104**, 8821 (1996).