AIP | The Journal of Chemical Physics

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Citation: The Journal of Chemical Physics **100**, 8700 (1994); doi: 10.1063/1.466725
View online: http://dx.doi.org/10.1063/1.466725
View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/100/12?ver=pdfcov
Published by the AIP Publishing

Interatomic distances for some first row transition element dichlorides isolated in cryogenic matrices using x-ray absorption fine structure spectroscopy

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(Received 27 December 1993; accepted 7 February 1994)

X-ray absorption fine structure (XAFS) data for several $3d$ transition metal dichlorides isolated in nitrogen, argon, or methane matrices have been collected and analyzed. The bond lengths obtained are in reasonable agreement with those from vapor phase electron diffraction. The results are briefly discussed with reference to Badger's rule extended to triatomics.

I. INTRODUCTION

The molecular structures of the monomeric halides of the transition elements are experimentally and theoretically challenging. In 1979 Drake and Rosenblatt[1] reviewed the data on the dihalides and trihalides, the majority of the experimental results arising from gas phase electron diffraction or spectroscopic studies of species isolated in cryogenic matrices. Gas phase electron diffraction formally yields all internuclear distances in a molecule. However, the raw data represent an average over all thermal vibrations and all species in the vapor.[2] Molecules isolated in an inert host matrix can be studied spectroscopically, the most frequently used technique being infrared absorption. When coupled with partial isotopic substitution this can yield the point group of the molecule and an estimate of bond angles. Alternatively, for open shell molecules electron paramagnetic resonance[3] can be used to obtain information on the electronic ground state. Inevitably, the matrix will affect the properties of the guest molecule. However, it is worth remembering that all single crystal x-ray structural investigations are subject to intermolecular interactions. Finally, we should note that in a very recent experiment[4] using laser induced fluorescence (LIF) spectroscopy under high resolution in a "cooled" molecular beam it has been shown that $NiCl_2$ is linear to within 4° in an excited electronic state and there is compelling evidence that it is also linear in its ground state. For the ground state[4] $r''_o = 2.056\ 07(13)$ Å while the electron diffraction value[5] is $r_e = 2.056(7)$ Å.

X-ray absorption fine structure (XAFS) spectroscopy of matrix isolated species can ideally give all internuclear distances from the absorbing atom, although the need to use less absorbing matrices renders the guest–host distances less reliable. For example, an argon matrix has a penetration depth of only 153 μm at the Cr K edge (assuming that it is 0.1% transmitting) although this increases steadily up to 583 μm at the Zn K edge. Further, the similarity of the backscattering phase and amplitude of Ar and Cl is a severe disadvantage as it is almost impossible to tell them apart. In the experiments to be described here, argon was only used for the heavier elements. Methane is an excellent matrix gas from the point of view of collection of XAFS data and earlier infrared (IR) work suggests that it does not interact strongly with the guest molecules.[6] We also studied some species in nitrogen matrices because of the evidence that considerable intermolecular interactions can occur between guest and host.[7]

II. EXPERIMENTAL SECTION

Iron (II) chloride and nickel (II) chloride were prepared from the reaction of high purity metal wire or foil (Goodfellows) with HCl gas (BDH 99.6%) and stored either in ampoules or a desiccator until loaded into the furnace assembly. The $CrCl_2$ was prepared *in situ* from the reaction of AgCl with Cr metal at ca. 650 °C. $ZnCl_2$ (BDH) was dried at 100 °C and sublimed under vacuum before loading into the furnace. The anhydrous or sublimed materials were loaded into the resistively heated silica furnace and degassed until a faint bloom was observed on the cooler parts of the water cooled vacuum jacket. The deposition temperatures (°C) were *approximately* as follows: Cr, 650; Fe, 450; Ni, 450; Zn, 220 and deposition times were of the order of 4–5 hours, the deposition being monitored by the increase in the x-ray fluorescence yield. The matrix gases N_2 (Air Products, BOC; high purity), Ar (Air Products, BOC; high purity), and CH_4 (BOC Research Grade) were all used as supplied.

The apparatus used for the matrix isolation XAFS experiments has been described previously[8] and consists of a high purity aluminium (Goodfellows, 0.25 mm, 99.995%) central deposition substrate maintained at ca. 9–10 K by a closed cycle refrigerator (APD Cryogenics DE204SL) mounted in an aluminium vacuum shroud. In order to mask any impurities in/on the aluminium, it was pretreated (before deposition) with a thin film of krypton or argon (for the iron edge) as described previously.[9,10] X-ray absorption spectra were measured in fluorescence mode using an Ar/He filled ion chamber to monitor I_0 and a Tl-doped NaI crystal scintillator to monitor I_f. Typically, four to eight spectra were

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0021-9606/94/100(12)/8700/6/$6.00

recorded and averaged. The matrices were laid down under conditions similar to those used in infrared experiments (using a dry air purged PE983G spectrometer operating in the range 4000–200 cm^{-1} [6,9]) recorded prior to the XAFS measurements in order to optimize the deposition conditions, where it could be shown that no polymeric species were detectable.

The XAFS data were collected on station 8.1 of the SERC Daresbury Laboratory Synchrotron Radiation Source (SRS) using Si[111] and Si[220] order sorting double crystal monochromators at 50% harmonic rejection and with a platinum focusing mirror. The SRS operated at 2 GeV with beam currents in the range 180–280 mA, and data were collected at the metal K edges.

III. DATA ANALYSIS

Background subtraction was carried out using PAXAS[11] by fitting the pre-edge region to a quadratic polynomial and subtracting this part from the whole spectrum. The atomic component of the oscillatory part of the spectrum was approximated using high order (typically six) polynomials and optimized by minimizing the chemically insignificant shells (<1 Å) in the Fourier transform. Curve fitting utilized the single scattering curved wave theory in the SERC Daresbury Laboratory EXCURV90 program,[12] and the phase shifts and back scattering factors were calculated by the usual *ab initio* methods.[12] The value of AFAC (shake up/shake off term) was set to the values determined previously for metal foils of Cr, 0.84;[13] Fe, 0.74;[9] Ni, 0.82;[14] and Zn, 0.85.[14]

The XAFS data were all analyzed in the same way. The first step was to determine the nature and number of the backscatterers in the first shell of the Fourier transform by Fourier filtration of this shell. Initially, it was assumed to be composed of chlorine atoms and the phase and amplitude of the XAFS confirmed this in each case. The residual (experiment minus theory) was checked to see if any other shells were present and in each case no significant features were observed. The occupation number for the metal chlorine shell (N_{M-Cl}) was determined by calculating contour maps (in terms of the R factor) of the Debye–Waller factor vs the VPI parameter (lifetime of the final state) for a range of values (1–4) of chlorine atoms. The criterion for judging the occupation number not only included the value of the R factor, but whether the Debye–Waller factor and VPI fell within "reasonable" values observed for similar systems. For all the systems except $CrCl_2/N_2$ the value of VPI was unreasonable for all occupation numbers except two. In this manner VPI was fixed for each system (Fe, −3.0 eV; Ni, −3.75 eV, Zn, −4.0 eV). Only in the case of chromium was the minimum poorly defined where a range of occupation numbers, Debye–Waller, and VPI parameters gave minima. Therefore, the value of VPI chosen (−2.0 eV) was that used previously[13] for matrix isolated CrO_2Cl_2. Having "solved" the first shell, the remainder of the features in the data were investigated using both the raw data and Fourier filtration, by comparing the quality of fit on changing the outlying backscatterers from matrix material to chlorine or metal. In particular, use of the sine (imaginary) Fourier transform was used to check not only the position of the features in the Fourier transform but also their phase. In each case the shells were best fit by the matrix host, indicating that monomeric species had been isolated. In order to determine the occupation numbers of these weaker features maps were calculated of occupation number vs Debye–Waller factor, and as to be expected a range of values fitted the data. Therefore, the Debye–Waller factor and occupation number were refined in turn and "reasonable" values chosen. For $ZnCl_2$ isolated in argon, the Debye–Waller factor for the Zn···Ar shell was set at 0.035 $Å^2$ (as determined previously for Kr in an Ar matrix[8]) and the occupation number was then refined. It should be borne in mind that the errors associated with the occupation numbers of these shells ($N_{M\cdots h}$) are quite large (typically ±3), therefore they are really only a guideline to high or low occupation number. As a number of shells of matrix host are anticipated it should also be remembered that these could effectively cancel each other out, so the absence of evidence should not be taken as evidence of absence.

The accuracy of the bond lengths arising from systematic errors in data acquisition and analysis is estimated to be ±1.5% for *well-defined* coordination shells.[15]

IV. RESULTS AND DISCUSSION

The refined XAFS parameters are shown in Table I together with vapor phase electron diffraction values for comparison. A representative XAFS spectrum and its corresponding Fourier transform for $ZnCl_2$ in a nitrogen matrix is shown in Fig. 1. The Fourier transform gives *approximately* the interatomic distances, but in order to obtain accurate data it is necessary to introduce phase shift terms and use a least-squares refinement procedure.

The Fourier transforms of the $ZnCl_2$ XAFS spectra in argon and nitrogen (Fig. 1) show strong features (after phase-shift correction) at 2.05(3) Å and 2.08(3) Å, respectively, which are both best fit by two chlorine atoms. These values should be compared with $r_g=2.072(4)$ Å obtained from gas phase electron diffraction.[16] The change in bond length of 0.03 Å between argon and nitrogen matrices is reflected in a change in vibrational frequency from 510.1 to 485.5 cm^{-1} for $^{64}Zn^{37}Cl_2$.[7] The weaker features to longer distance are associated with the host matrix. Similar results were obtained for $FeCl_2$. In a methane matrix the only feature is at 2.16(3) Å while in nitrogen the principal feature is at a slightly greater distance of 2.21(3) Å together with weaker features from the matrix environment. In this case for a drop in frequency of 16 cm^{-1} from methane to nitrogen there is an increase in bond length of 0.05 Å.

The case of nickel dichloride is complicated by indications that $NiCl_2$ is bent in a nitrogen matrix.[7] For a methane matrix the main shell is at 2.12(3) Å while in a nitrogen matrix this shell occurs at 2.15(3) Å, there being one and two additional shells, respectively. Finally, for $CrCl_2$ in nitrogen the main shell is at 2.26(3) Å.

The values of the bond lengths we have determined using XAFS are in reasonable agreement with the available electron diffraction vapor phase values. However, it is difficult to predict whether a thermally averaged gas phase molecule or a molecule isolated in a host matrix would be expected to have the greater bond distance. In addition, it is

TABLE I. Refined XAFS structural parameters for some metal dichlorides in cryogenic matrices.[a,b]

	$r_{\text{M-Cl}}/\text{Å}$[c]	$2\sigma^2_{\text{M-Cl}}/\text{Å}^2$[d]	$N_{\text{M-Cl}}$[e]	$r_{\text{M}\cdots h}/\text{Å}$[f]	$2\sigma^2_{\text{M}\cdots h}/\text{Å}^2$	$N_{\text{M}\cdots h}$	E_0/eV	VPI/eV	AFAC	FI[g]	R[h]
$CrCl_2/N_2$[i]	2.257(2)	0.0055(2)	2	3.371(6)	0.0123(20)	5	22.0(3)	−2.0	0.84	3.195	25.36
$CrCl_2$/ED	2.207(10)[j] 2.18(2)[k]		2 2								
$FeCl_2/CH_4$[i]	2.156(3)	0.0077(4)	2				18.8(6)	−3.0	0.74	3.548	32.36
$FeCl_2/N_2$[i]	2.207(2)	0.0055(2)	2	3.233(7) 4.398(7)	0.0284(20) 0.0010(13)	7 3	11.9(3)	−3.0	0.74	1.858	21.38
$FeCl_2$/ED[l]	2.151(5)		2								
$NiCl_2/CH_4$[i]	2.123(3)	0.0070(3)	2	2.938(16) 3.374(14)	0.0385(58) 0.0323(44)	6 9	24.4(6)	−3.75	0.82	7.505	36.31
$NiCl_2/N_2$[i]	2.145(2)	0.0088(2)	2	2.837(12) 3.341(7)	0.0224(36) 0.0186(14)	2 6	28.3(4)	−3.75	0.82	2.235	25.33
$NiCl_2$/ED[l]	2.076(4)		2								
$ZnCl_2$/Ar[i]	2.053(2)	0.0059(3)	2	3.101(10)	0.0506(60)	13	14.0(6)	−4.5	0.85	6.616	38.01
$ZnCl_2/N_2$[i]	2.081(2)	0.0053(3)	2	4.078(13)	0.0184(27)	12	15.6(6)	−4.5	0.85	6.929	33.71
$ZnCl_2$/ED[m]	2.072(4)		2								

[a] Standard deviations in parentheses.
[b] ED are vapor phase electron diffraction r_g values.
[c] Estimated systematic errors are ±1.5% for well defined coordination shells (Ref. 15).
[d] $2\sigma^2$ is the Debye–Waller factor.
[e] N is the shell occupation number.
[f] h is the matrix host, i.e., N, C, or Ar.
[g] $FI=\Sigma_i\{(\chi_i^T(k)-\chi_i^E(k))(k^3)\}^2$.
[h] $R=[\int k^n|(\chi^T(k)-\chi^E(k))|dk/\int k^n|(\chi^E(k))|dk]\times 100$.
[i] This work.
[j] Reference 21.
[k] Reference 22.
[l] Reference 5.
[m] Reference 16.

clear from the iron and zinc dichloride experiments that the XAFS bond lengths are affected by the matrix, presumably due to subtle changes in the potential energy surface, so that direct comparison between vapor and matrix values is not possible. Therefore, we investigated the possibility of using Badger's rule as an aid to assessing the reliability of the XAFS data.

Badger's rule[17] relating $k_e^{-1/3}$ with r_e, (where k_e and r_e are the equilibrium force constant and bond length, respectively) has been extensively applied to *diatomics* and recently was applied to third row transition metal monoxide species.[18] In order to assess the appropriateness of Badger's rule for triatomics such as transition metal dichlorides we first examined the case for the bond lengths determined by vapor phase electron diffraction. In the case of the dichlorides under discussion the gas phase values of the antisymmetric stretching frequency, ν_3, are not known accurately across the whole series but there is argon matrix literature data available[19] for all of them except $CuCl_2$. Using these values with a simple valence force field (SVFF) and assuming linearity, a force constant k_e can be calculated. In Fig. 2(a) we show a "Badger's rule" plot for the first row transition metal dichlorides using the argon matrix vibrational values for ν_3 and the electron diffraction r_g data[20] [r_g is the thermally averaged distance at the temperature of the experiment and has been used rather than r_e (equilibrium distance) because of the availability of the data]. (The points for VCl_2 and $CrCl_2$ have been omitted because of uncertainties in the reliability of the data.[21–24]) The least-squares fit line is based on all the points and has a goodness of fit (r^2) of 94.4%. This figure therefore shows that "Badger's rule" plots can be useful in assessing bond length and spectroscopic experimental data for the transition metal dichlorides.

Figure 2(b) shows the results of our XAFS studies where the bond length is plotted against $k_e^{-1/3}$ for the dichlorides in the relevant matrices. The IR data for argon and nitrogen matrices have been taken from the literature.[7] The methane matrix data are $FeCl_2$, 462.6 cm^{-1}; and $NiCl_2$, 510.1 cm^{-1}. The least-squares fit uses all the points except that for $NiCl_2$ in a dinitrogen matrix, where special circumstances apply.[7] The goodness of fit (r^2) for this plot (94.5%) is almost identical to that for the electron diffraction values and if the $NiCl_2$ in methane point is removed from the calculation, r^2 becomes 99.0%. The vibrational frequency of 510.1 cm^{-1} for the $NiCl_2/CH_4$ system implies a bond length of 2.09 Å from this plot compared to the 2.12 Å obtained from the XAFS experiment, which is just on the edge of the error limits.

The value of the bond length for $CrCl_2$ in solid nitrogen (2.26 Å) is in very good compliance with that expected from

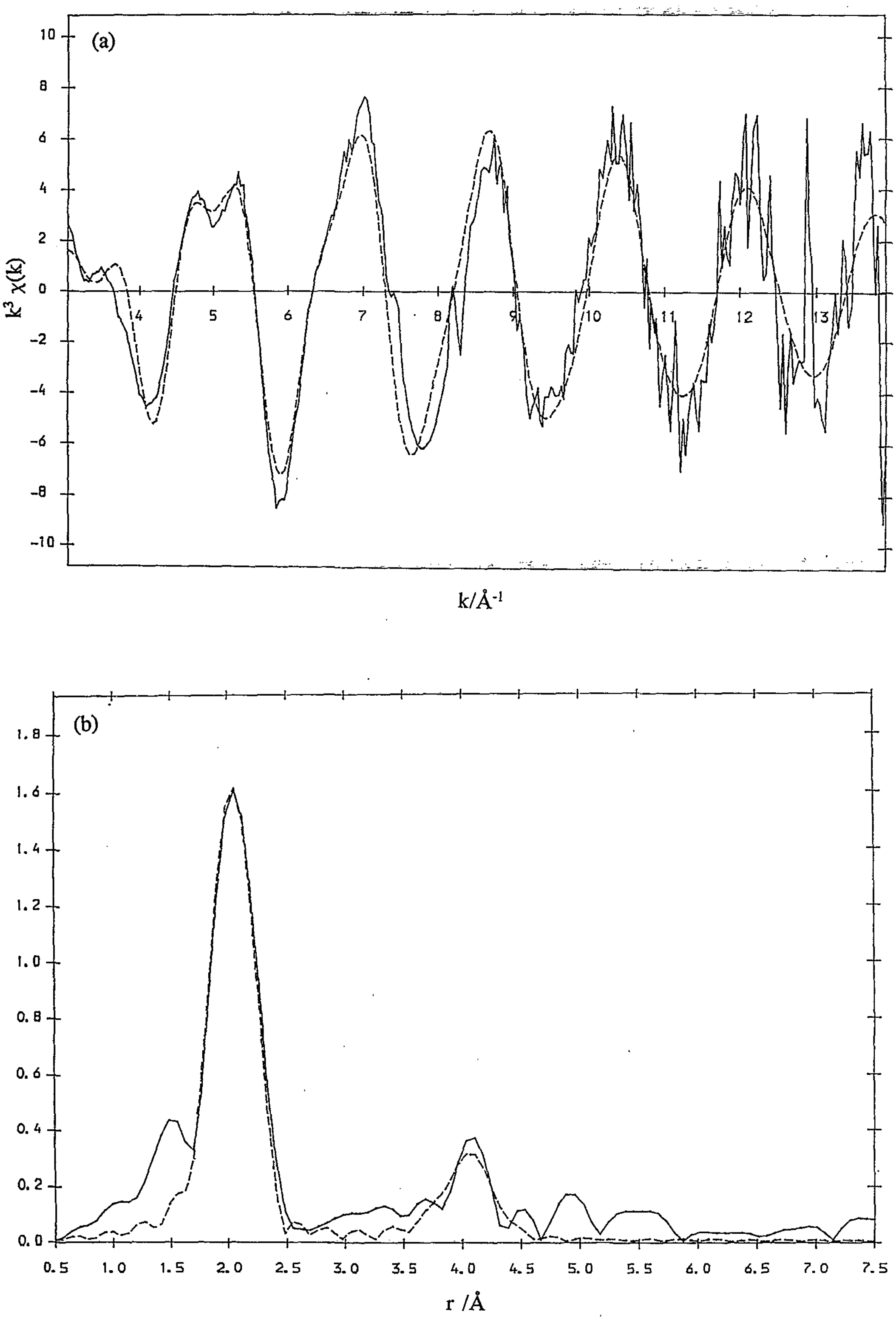

FIG. 1. XAFS (a) and Fourier transform (b) for $ZnCl_2$ isolated in a nitrogen matrix at ca. 10 K. Solid line experiment, dotted line curved wave theory.

the least-squares plot for the matrix data and therefore indicates that the ill defined Cr–Cl occupation number is not due to the presence of oligomers or higher halides but to a shallow minimum.

The point for $NiCl_2$ in solid nitrogen is a long way off the least-squares line and lies on the side which implies that the observed bond length (2.15 Å) is too short (the extrapolated value is 2.22 Å). This, however, is expected because we have recently shown[7] that the bond angle derived from both the nickel and chlorine isotope patterns on ν_3 of $NiCl_2$ in a nitrogen matrix is ca. 130° compared to approximately 180° in argon or methane matrices. As the bond angle is reduced the *calculated* force constant increases and this is marked as ♦ on Fig. 2(b) (1.90 mdyne/Å for 130°). We found no evidence of a ν_{NN} stretching mode in the infrared spectra[7] and in these XAFS studies there is no evidence of a short Ni–N bond, both of which indicate that the significant change in the infrared spectrum is not due to bonded dinitrogen. We do, however, observe an Ni···N distance at ca. 2.84 Å with a low occupancy of ca. two nitrogen atoms.

If one assumes that the $NiCl_2$ unit is indeed linear in a nitrogen matrix and that the apparent bond angle of 130° is due to interaction of the nickel with that matrix, then the *effective masses* of the central nickel atom required to reproduce the *observed* $^{58}\mathrm{Ni}\rightarrow{}^{60}\mathrm{Ni}$ nickel isotope shifts[7] are 62.8 and 64.8 (for $\mathrm{Ni}^{37}\mathrm{Cl}_2$) compared to 58.6 and 60.6 (for $\mathrm{Ni}^{37}\mathrm{Cl}_2$) for the argon data. Although there is no precedent for such behavior and the isotope shift method is considered to be a reliable means of determining bond angles for matrix isolated species, we felt that it was worth doing some elementary calculations. Using the *F* and *G* matrices derived by Beattie *et al.*[25] for D_{4h} L_2MX_4 species with N_2 as a point mass and a deformation frequency one tenth that of the stretching frequency[26,27] for NiAr^+, the isotope shifts could only be modeled by using an interaction force constant some ten times the deformation force constant. On balance we therefore favor the interpretation that $NiCl_2$ is strongly nonlinear in a nitrogen matrix.

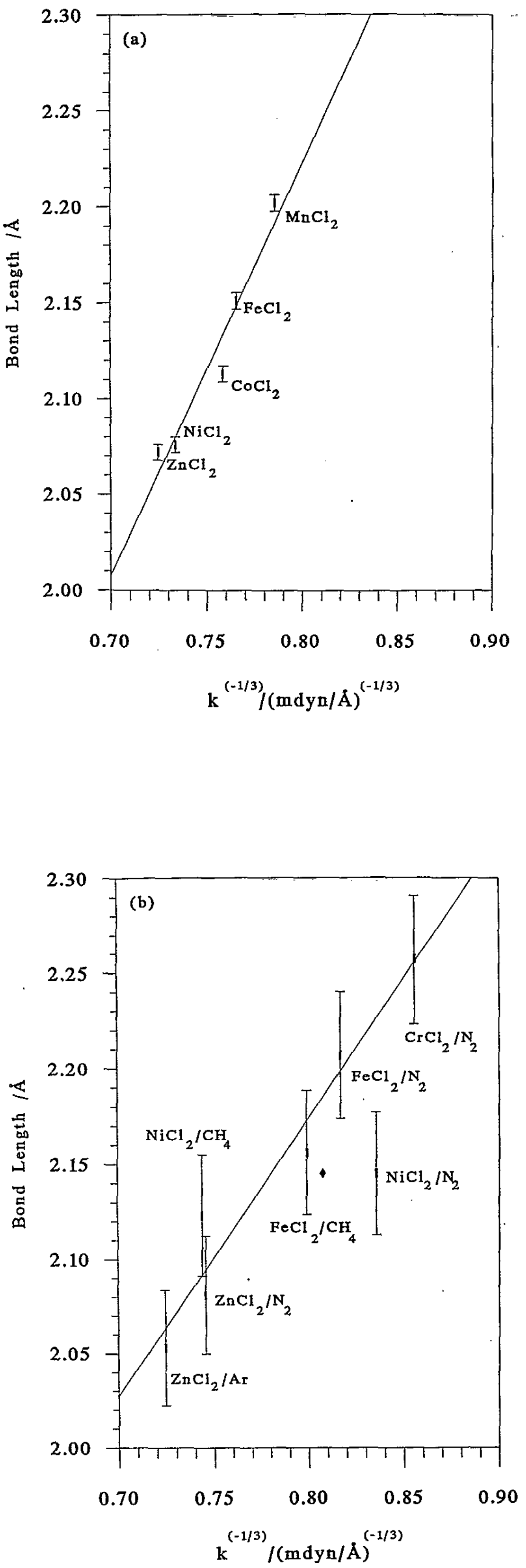

FIG. 2. Badger's rule plot of bond length vs $k^{-1/3}$ for first row transition metal dichlorides. (a) vapor phase electron diffraction, (b) matrix isolated XAFS. (k=SVFF force constant assuming linearity.)

V. CONCLUSIONS

We have used XAFS to determine intramolecular and intermolecular bond lengths in a range of first row transition metal dichlorides isolated in cryogenic matrices. The data obtained are in reasonable agreement with vapor phase electron diffraction data. We have also utilized modified Badger's rule plots to assess the reliability of our data, having first demonstrated its applicability for electron diffraction data.

The metal–matrix distances give values of contact distances that are not determinable by other means and give an insight into host–guest interactions. However, the values obtained from these experiments should be treated with caution because a number of competing factors will affect the outcome, not the least of which is the problem of overlapping shells cancelling each other out.

ACKNOWLEDGMENTS

We acknowledge the help of Dr. W. Levason and Dr. J. S. Ogden with some of the data collection, the SERC for financial support, especially for the provision of an Advanced Fellowship (N.A.Y.), the Leverhulme Trust for a Fellowship (I.R.B.) and the Director of Daresbury Laboratory for the provision of Synchrotron and computing facilities.

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