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Short Communication

Molecular Parameters of Gaseous $CdCl_2$ from Electron Diffraction and Vibrational Spectroscopic Data

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The available information on the molecular structures of the gaseous monomeric Group 12 dihalides, MX_2(g), M = Zn, Cd or Hg and X = F, Cl, Br or I, is incomplete and, in part, contradictory.

Büchler *et al.*[1] have studied the electric deflection of molecular beams of the difluorides ZnF_2, CdF_2 and HgF_2, the dichlorides $ZnCl_2$ and $HgCl_2$, and HgI_2. All were found to be nonpolar, and consequently should have linear or pseudolinear equilibrium structures.

Gas-phase electron diffraction (GED) investigations also suggest linear equilibrium structures for Group 12 dihalides: The first studies of $CdCl_2$ by the visual method recommended a linear configuration;[2,3] an investigation of $HgCl_2$ by standard analysis including 'shrinkage correction' indicated a linear structure;[4] the vibrational potential functions of HgI_2 have been determined from GED data under the assumption of a linear equilibrium geometry;[5,6] recent studies of ZnX_2 (X = Cl, Br or I)[7] and $CdCl_2$,[8] where the data were analysed under the assumption of a harmonic molecular force field and rectilinear motion of the terminal atoms during the bending motion[9] (the so-called harmonic rectilinear approximation), indicated that the equilibrium structures were linear.

As pointed out by Girichev *et al.* and Gershikov in their studies of ZnF_2[10] and $CdBr_2$,[11] respectively, the description of the bending vibration in terms of rectilinear motion of the terminal atoms is suspect for molecules undergoing large-amplitude bending. Instead they analysed their data using a program based on curvilinear motion of the terminal atoms as well as an *anharmonic* potential for the bending vibration. The joint analysis of GED and spectroscopic data yielded a linear equilibrium structure for $CdBr_2$.[11] For ZnF_2 a slightly bent equilibrium structure could not be excluded.[10] Finally, a similar study of CdI_2 has yielded a linear equilibrium structure.[12]

Loewenschuss and coworkers[13–16] have recorded the infrared and Raman spectra of several Group 12 dihalides in inert gas matrices and assigned the symmetric and asymmetric stretching modes ν_1 and ν_3. These modes were calculated from the force constants f_r and f_{rr} and the valence angle α, and these parameters were varied under the condition that $f_{rr} < 0.1 f_r$ to reproduce both band positions and isotopic fine structure. Acceptable agreement between observation and calculations were obtained with valence angles in the following ranges: $ZnCl_2$ (165–180°); $ZnBr_2$ (162–169°); ZnI_2 (148–180°); $CdCl_2$ (166–180°); $CdBr_2$ (155–180°); $HgCl_2$ (140–148°); $HgBr_2$ (127–150°). Loewenschuss' analysis thus indicates that three molecules, *viz.* $ZnBr_2$, $HgCl_2$ and $HgBr_2$, are significantly bent in the gas phase. One of these, $HgCl_2$, has been found to be linear by molecular beam techniques[1] and by gas-phase electron diffraction,[4] while another, $ZnBr_2$, is linear by GED.[7]

In this communication we present the results of the analysis of GED data[8] for $CdCl_2$ based on an anharmonic bending potential and curvilinear motion of the Cl atoms. The theory of the analysis has been developped by Gershikov and Spiridonov[17] and applied for the first time to some transition metal difluorides.[18]

The internuclear distance Cd–Cl, which corresponds with the minimum of the potential function in this approximation, is called r_e^{ch}. The applied bending potential function has the form of eqn. (1), where k_2 and k_4 are

$$V = \tfrac{1}{2} k_2 \rho^2 + k_4 \rho^4 \qquad (1)$$

the quadratic and quartic force constants and $\rho = \pi - \alpha$ is the non-rigid variable with the bonding angle α in radians. For positive k_2 values the potential function has one

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minimum, whereas for negative k_2 values (but $k_4 > 0$) it has two equivalent minima with $\rho_e = \pm(-k_2/4k_4)^{1/2}$.

The experimental electron diffraction data have been analysed independently from spectroscopically obtained frequencies. The sum G in eqn. (2) has been minimized,

$$G = \sum_i p_i [s_i M(s_i)^{\exp} - \gamma s_i M(s_i)^{\mathrm{calc}}]^2 \tag{2}$$

where γ is a scale factor and p_i are the weighting factors: The molecular intensity curve, obtained with a nozzle-to-plate distance of 25 cm, has the constant relative weight of 0.4 in comparison with the curve for the 50 cm distance (more details are given in Ref. 8). The optimized parameters are the internuclear distance r_e^{ch}(Cd–Cl), the stretching force constants f_r and f_{rr}, and also the bending force constants k_2 and k_4. Owing to the strong correlation of f_r with f_{rr} (correlation coefficient -0.97), f_{rr} has been fixed at the spectroscopically obtained value[16] -0.014 mdyn/Å. The resulting parameters for $CdCl_2$ are given and compared with literature values in Table 1. The force constants and frequencies agree reasonably well with the spectroscopic data.

The resulting quadratic force constant k_2 is positive, which is consistent with a linear equilibrium configuration. However, the uncertainty does not exclude negative k_2 values, a result which corresponds with a bond angle deviation up to 15° from linearity. The estimated maximal possible potential barrier between both equivalent minima is in the order of the ground vibrational level, whose energy has been determined from k_2 and k_4 by numerical solution of the Schrödinger equation with the Hamiltonian (8) given in Ref. 17, using the Numerov–Cooley algorithm.[19] This means that the $CdCl_2$ molecule cannot be a typically bent molecule.

Table 1. Molecular parameters of $CdCl_2$.

Parameter	This work	Literature
r_e^{ch}(Cd–Cl)/Å	2.279(4)[a]	
r_e(Cd–Cl)/Å	2.266(6)	
$\angle_e$(Cl–Cd–Cl)/°	180(15)[b]	166–180[c]
f_r/mdyn/Å	2.00(14)[d]	2.234–2.256[c]
f_{rr}/mdyn/Å	−0.014[e]	−0.014–0.008[c]
k_2/mdyn Å	0.17(23)[d]	
k_4/mdyn Å	0.00(28)[d]	
ν_1/cm^{-1}	309(11)[f]	329.8(75)[g]
ν_2/cm^{-1}	72[h]	83(2),[i] 88(1)[j]
ν_3/cm^{-1}	397(14)[f]	419.0(25),[k] 427[l]

[a]Estimated errors σ_t for internuclear distances r in units of last significant figures calculated according to $\sigma_t = \{(2\sigma_{LS})^2 + \sigma_s^2 r^2\}^{1/2}$, where σ_{LS} is the least-squares standard deviation and the experimental scale error $\sigma_s = 0.001$. [b]Estimated error as discussed in text. [c]Ref. 16. [d]Estimated error for force constants $2\sigma_{LS}$ in units of last significant figures. [e]Fixed (see text). [f]Uncertainties estimated from uncertainty of f_r. [g]Raman spectrum in krypton matrix.[13] [h]Estimated error 15 cm^{-1}. [i]Infrared spectrum in the gas phase.[23]. [j]Infrared spectrum in a krypton matrix.[24] [k]Infrared spectrum in a krypton matrix.[14] [l]Infrared spectrum in the gas phase.[25]

Table 2. Different types of internuclear distances r(Cd–Cl) (in Å) for $CdCl_2$.

Type	Value[a]	Ref.
r_a	2.282(4)	Ref. 8
r_g	2.284(4)	This work
r_e^{ch}	2.279(4)	This work
r_e	2.266(6)	This work
r^b	2.21(2)	Ref. 2
r^b	2.23(3)	Ref. 3

[a]Estimated errors in this work according to footnote [a] in Table 1. [b]Visual method, type not specified.

The value of the corresponding equilibrium bond length r_e(Cd–Cl) may be estimated from r_e^{ch}(Cd–Cl) values taking into account the Morse-type anharmonic stretching contribution,[11,20] eqn. (3), where a is the Morse

$$r_e(\mathrm{Cd–Cl}) = r_e^{\mathrm{ch}}(\mathrm{Cd–Cl}) - \tfrac{3}{2} a l^2(\mathrm{Cd–Cl}) \tag{3}$$

constant for the diatomic molecule CdCl. According to Ref. 21 it can be calculated from eqn. (4). Here μ are the

$$a = (8\pi^2 c\mu\omega_e x_e/h)^{1/2} \tag{4}$$

reduced mass and $\omega_e x_e$ the anharmonic constant ($\omega_e x_e = 1.3$ cm^{-1}).[22] The estimated value $a = 1.45$ Å^{-1} for $CdCl_2$ agrees well with the estimated value $a = 1.42$ Å^{-1} for $CdBr_2$[11] and with the experimental value $a = 1.2 \pm 0.4$ Å^{-1} for CdI_2.[12] The estimate for r_e(Cd–Cl) is 2.266(6) Å.

Table 2 compares different types of internuclear distances r(Cd–Cl) and shows that the anharmonic correction is greater than the estimated experimental error.

In total the best agreement has been obtained for a linear model, but a quasilinear model with a bond angle between 165 and 180° and a low potential barrier to linearity cannot be ruled out. This conclusion agrees with the uncertain bond angle range (166–180°) determined from isotopic shifts of vibrational frequencies.[16] It also supplements the conclusion that ZnF_2[10] may have a weakly pronounced minimum in the bending potential.

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