Short Communication

Molecular Parameters of Gaseous CdCl₂ 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, MX₂(g), M = Zn, Cd or Hg and X = F, Cl, Br or I, is incomplete and, in part, contradictory. Bühler et al.1 have studied the electric deflection of molecular beams of the difluorides ZnF₂, CdF₂, and HgF₂, the dichlorides ZnCl₂ and HgCl₂, and HgI₂. 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 CdCl₂ by the visual method recommended a linear configuration;2,3 an investigation of HgCl₂ by standard analysis including ‘shrinkage correction’ indicated a linear structure;4 the vibrational potential functions of HgI₂ have been determined from GED data under the assumption of a linear equilibrium geometry;5,6 recent studies of ZnX₂ (X = Cl, Br or I)7 and CdCl₂,8 where the data were analysed under the assumption of a harmonic molecular force field and rectilinear motion of the terminal atoms during the bending motion9 (the so-called harmonic rectilinear approximation), indicated that the equilibrium structures were linear.

As pointed out by Giričev et al. and Gershikov in their studies of ZnF₂,10 and CdBr₂,11 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 CdBr₂.11 For ZnF₂ a slightly bent equilibrium structure could not be excluded.10 Finally, a similar study of CdI₂ has yielded a linear equilibrium structure.12

Loewenschuss and coworkers13–16 have recorded the infrared and Raman spectra of several Group 12 dihalides in inert gas matrices and assigned the symmetric and asymmetric stretching modes ν₁ and ν₃. These modes were calculated from the force constants ƒᵣ and ƒᵟ, and the valence angle α, and these parameters were varied under the condition that ƒᵣ < 0.1ƒᵟ to reproduce both band positions and isotopic fine structure. Acceptable agreement between observation and calculations were obtained with valence angles in the following ranges: ZnCl₂ (165–180°); ZnBr₂ (155–168°); ZnI₂ (148–180°); CdCl₂ (166–180°); CdBr₂ (127–150°). Loewenschuss’ analysis thus indicates that three molecules, viz. ZnBr₂, HgCl₂ and HgBr₂, are significantly bent in the gas phase. One of these, HgCl₂, has been found to be linear by molecular beam techniques1 and by gas-phase electron diffraction,4 while another, ZnBr₂, is linear by GED.7

In this communication we present the results of the analysis of GED data8 for CdCl₂ based on an anharmonic bending potential and curvilinear motion of the Cl atoms. The theory of the analysis has been developed by Gershikov and Spiridonov17 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 rᵫ. The applied bending potential function has the form of eqn. (1), where k₂ and k₄ are

\[ V = \frac{1}{2} k_2 \rho^2 + k_4 \rho^4 \]  

(1)

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

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minimum, whereas for negative $k_z$ values (but $k_z > 0$) it has two equivalent minima with $\rho_s = \pm k_z/4k_e$.

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

$$G = \sum p_i [s_i M(s_i)^{exp} - s_i M(s_i)^{calc}]^2$$

where $\gamma$ 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 $r_{eq}^{0}$(Cd–Cl), the stretching force constants $f_s$ and $f_r$, and also the bending force constants $k_2$ and $k_3$. 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 $-0.014$ mdyn/Å. The resulting parameters for CdCl₂ 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 $k_3$ values, a result which corresponds with a bond angle deviation up to $15^\circ$ 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 $k_3$ by numerical solution of the Schrödinger equation with the Hamiltonian (8) given in Ref. 17, using the Numerov–Cooley algorithm. This means that the CdCl₂ molecule cannot be a typically bent molecule.

Table 1. Molecular parameters of CdCl₂.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>This work</th>
<th>Literature</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_{eq}^{0}$(Cd–Cl) Å</td>
<td>2.278(4)*</td>
<td></td>
</tr>
<tr>
<td>$r_0$(Cd–Cl)/Å</td>
<td>2.266(6)</td>
<td></td>
</tr>
<tr>
<td>$\xi$(Cl–Cd–Cl)/°</td>
<td>180(15)°</td>
<td>166–180°</td>
</tr>
<tr>
<td>$f_s$/mdyn/Å</td>
<td>2.00(14)°</td>
<td>2.234–2.256</td>
</tr>
<tr>
<td>$f_r$/mdyn/Å</td>
<td>-0.014°</td>
<td>-0.014–0.008</td>
</tr>
<tr>
<td>$k_2$/mdyn Å</td>
<td>0.17(23)°</td>
<td></td>
</tr>
<tr>
<td>$k_3$/mdyn Å</td>
<td>0.00(28)°</td>
<td></td>
</tr>
<tr>
<td>$v_a$/cm⁻¹</td>
<td>309(11)°</td>
<td>329.8(75°)</td>
</tr>
<tr>
<td>$v_b$/cm⁻¹</td>
<td>72°</td>
<td>83.2°, 88.1°</td>
</tr>
<tr>
<td>$v_c$/cm⁻¹</td>
<td>397(14)°</td>
<td>419.0(25), 427°</td>
</tr>
</tbody>
</table>

*Estimated errors $\sigma_i$ for internuclear distances $r_i$ in units of last significant figures calculated according to $\sigma_i = \{2(2\sigma_i^2 + \sigma_i^2)^{1.2}\}$, where $\sigma_i$ is the least-squares standard deviation and the experimental scale error $\sigma_i = 0.001$.

Table 2. Different types of internuclear distances $r$(Cd–Cl) (in Å) for CdCl₂.

<table>
<thead>
<tr>
<th>Type</th>
<th>Value*</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_s$</td>
<td>2.282(4)</td>
<td>Ref. 8</td>
</tr>
<tr>
<td>$r_o$</td>
<td>2.284(4)</td>
<td>This work</td>
</tr>
<tr>
<td>$r_{eq}^{0}$</td>
<td>2.279(4)</td>
<td>This work</td>
</tr>
<tr>
<td>$r_0$</td>
<td>2.266(6)</td>
<td>This work</td>
</tr>
<tr>
<td>$r_f$</td>
<td>2.21(2)</td>
<td>Ref. 2</td>
</tr>
<tr>
<td>$r_b$</td>
<td>2.23(3)</td>
<td>Ref. 3</td>
</tr>
</tbody>
</table>

*Estimated errors in this work according to footnote * in Table 1. Visual method, type not specified.

The value of the corresponding equilibrium bond length $r_s$(Cd–Cl) may be estimated from $r_{eq}^{0}$(Cd–Cl) values taking into account the Morse-type anharmonic stretching contribution, 11–20 eqn. (3), where $a$ is the Morse constant for the diatomic molecule CdCl. According to Ref. 21 it can be calculated from eqn. (4). Here $\mu$ are the

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

reduced mass and $\omega_a x_e$ the anharmonic constant ($\omega_a x_e = 1.3$ cm⁻¹). The estimated value $a = 1.45$ Å⁻¹ for CdCl₂ agrees well with the estimated value $a = 1.42$ Å⁻¹ for CdBr₂ 11 and with the experimental value $a = 1.2 ± 0.4$ Å⁻¹ for CdI₂. 12 The estimate for $r_s$(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. It also supplements the conclusion that ZnFCl₂ may have a weakly pronounced minimum in the bending potential.

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References

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