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Structural investigation of molecules in the vapour over beryllium dichloride using electron diffraction and mass spectrometric data

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Abstract

According to the data of simultaneous gas-phase electron diffraction (GED) and mass spectrometric (MS) experiments the vapour over beryllium dichloride at 547 K consists of monomeric and dimeric molecules in the ratio 97.5:2.5. Molecular parameters were refined for both molecules from GED data. The equilibrium structure of BeCl₂ is linear with the bond length $r_e^{\text{anh}}(\text{Be}-\text{Cl}) = 1.791(5)$ Å. The thermal-average bond length $r_g(\text{Be}-\text{Cl})$ is 1.798(4) Å. Relations between different kinds of the refined parameters (r_a , r_α , r_e^{h} , r_e^{ch} , r_e^{anh}) are discussed. Force constants and vibrational frequencies were obtained for this molecule from GED data alone. Assuming D_{2h} symmetry the following parameters were obtained for Be₂Cl₄: $r_g(\text{Be}-\text{Cl}_i) = 1.828(14)$ Å, $r_g(\text{Be}-\text{Cl}_b) = 1.968(20)$ Å, $\angle_\alpha(\text{Cl}_i-\text{Be}-\text{Cl}_b) = 134(4)^\circ$. The force constants and frequencies for the dimer were estimated.

Keywords: Beryllium dichloride; Gas-phase electron diffraction; Mass spectrometry

1. Introduction

The present work is a continuation of our systematic investigations of beryllium dihalides by means of gas-phase electron diffraction (GED) [1].

The first experimental structural data of BeCl₂ were obtained by Akishin and Spiridonov in 1957 [2] using the visual GED method, which yielded the parameters in low precision: $r(\text{Be}-\text{Cl}) = 1.75(2)$ Å and $\angle(\text{Cl}-\text{Be}-\text{Cl}) = 180(30)^\circ$. Büchler et al. [3] also concluded that the molecule is linear because they failed to observe the refocussing of the molecular beam in

the anisotropic electric field. In a further study Büchler and Klemperer [4] investigated the gas-phase infrared spectrum and assigned the bands at 482 and 1113 cm⁻¹ to the vibrational frequencies ν_2 and ν_3 , respectively. Two bands of the dimer Be₂Cl₄ were also observed. On the basis of the ν_3 value [4], Baikov [5] estimated the symmetrical stretching ν_1 to be 373 cm⁻¹ using a simple valence force field approximation. According to the matrix infrared data by Snelson [6,7], which were corrected for matrix shifts, ν_2 and ν_3 were 250 and 1135 cm⁻¹, respectively. The unobserved value of ν_1 was estimated to be 390 cm⁻¹ using the simple valence force field approximation. Snelson's data agree well with the results mentioned above except for the value of ν_2 .

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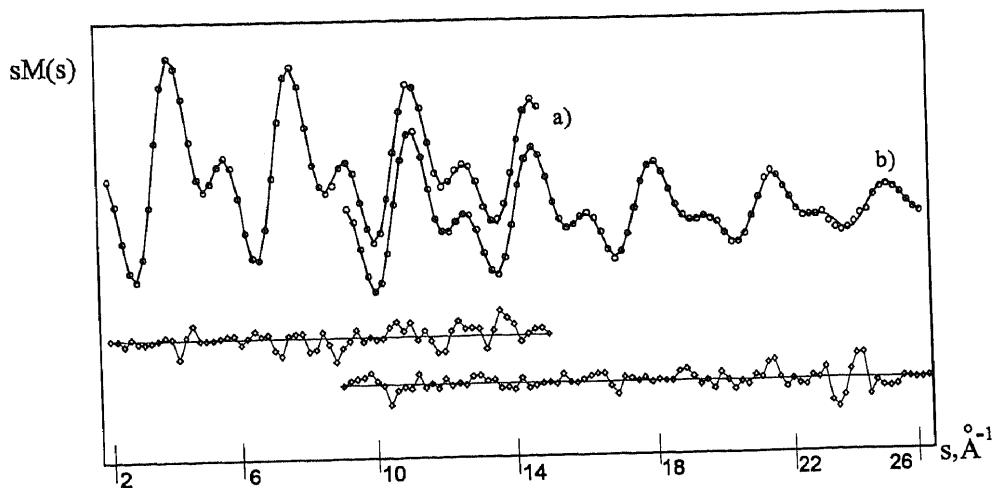


Fig. 1. Experimental (○) and theoretical (—) molecular intensity curves for long (a) and short (b) nozzle-to-plate distances and their difference curves (◇) (multiplied by 5).

The ab initio closed-shell SCF method combined with the energy gradient technique was applied by Hashimoto et al. [8] to study the structures of the monomer and dimer of beryllium dichloride. The authors predicted a linear configuration for BeCl_2 and D_{2h} symmetry for Be_2Cl_4 . The calculated bond lengths increased by up to 0.07 \AA when the basis set was changed from STO-3G to 3-21G. All vibrational frequencies of BeCl_2 and Be_2Cl_4 were obtained. However, the computed values are systematically higher (up to 15%) than the experimental ones [4,6,7] except

for the bending frequency ν_2 of BeCl_2 which is in good agreement with the experimental data [6].

Various authors [9-11] detected the dimeric molecule in the vapour over beryllium dichloride. Data by Ko et al. [11] indicated about 65 mol% dimer at 470 K, whereas Hildenbrand's mass spectrum suggested a largely monomeric saturated vapour with only a low percentage of dimer at 503 K [9].

In this work we present the results of the analysis of joint GED and MS experiments for saturated vapour over beryllium dichloride.

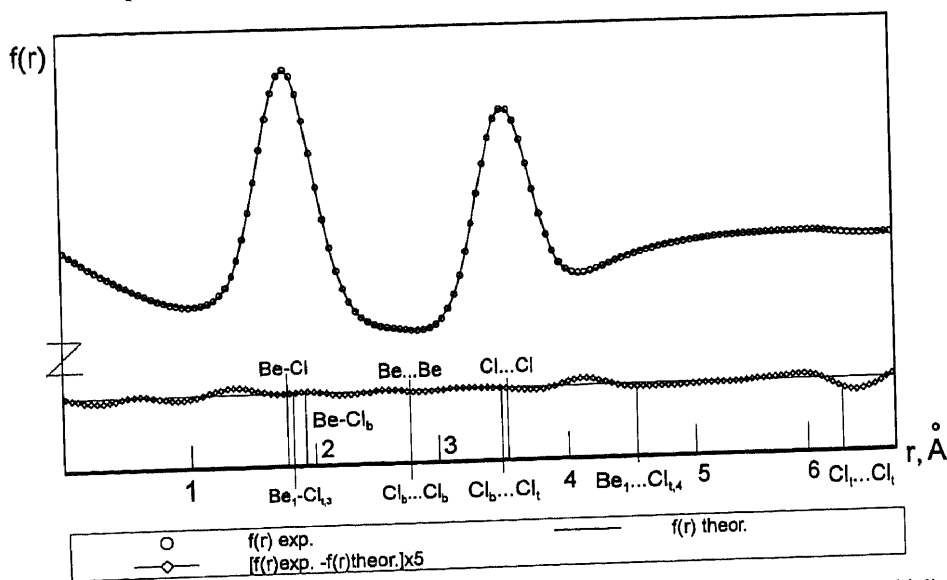


Fig. 2. Experimental (○) and theoretical (—) radial distribution curves and difference curve (◇) (multiplied by 5).

2. Experimental

The electron diffraction patterns of saturated vapour over beryllium dichloride were simultaneously recorded with the mass spectrometric data on a modified EMR-100/APDM-1 apparatus [12,13]. A commercial sample from Fluka Company with a purity of 97%(Cl) was used. The sample was vaporized at 547 K from a radiation-heated stainless steel cell with an effusion channel $0.6 \times 2.5 \times 4.0$ mm. The ratio of the surface area of vaporization to the square section of the effusion channel was about 200. Mass spectra were obtained at the ionization voltage 50 V in the range 0–800 a.m.u. They were recorded before and during the electron diffraction experiment.

The electron diffraction pattern was obtained at an accelerating voltage of 73.5 kV for the nozzle-to-plate distances $L_1 = 598$ mm and $L_2 = 338$ mm (four plates each selected). The vacuum in the diffraction chamber was held at 3.10^{-6} Torr during the experiment. The electron wavelength ($\lambda = 0.0444$ Å) was calibrated with crystalline ZnO powder. Optical densities were recorded on the MF-4 densitometer and processed by a program [14]. The experimental intensity curves $I(s)$ were obtained in the intervals $s = 2.2$ – 14.8 Å $^{-1}$ (L_1) and $s = 9.2$ – 26.2 Å $^{-1}$ (L_2) with the steps $\Delta s = 0.2$ Å $^{-1}$, where s is the standard variable of scattering. The resulting molecular intensity curves $sM(s)$ are displayed in Fig. 1. The radial distributions curves $f(r)$ are shown in Fig. 2. The atomic electron scattering factors (amplitudes and phases) were taken from tables [15].

3. Mass spectral analysis

Mass spectra were recorded before and during the electron diffraction experiment. The relative intensities were 2.0, 36.0, 100.0, 4.6 and 2.7 for the ion peaks of Be^+ , BeCl^+ , BeCl_2^+ , Be_2Cl_3^+ and Be_2Cl_4^+ , respectively. The mass spectra showed that the vapour does not contain only BeCl_2 . We assumed that the ions Be^+ , BeCl^+ and BeCl_2^+ came from the monomeric molecules, whereas the ions Be_2Cl_3^+ and Be_2Cl_4^+ originated in the dimeric molecules. This assumption is based on the data of Hildenbrand and Theard [9]. The ratio between the cross-sections of ionization for Be_2Cl_4 and BeCl_2 was assumed to be equal to 2.0.

According to this hypothesis the concentration of the dimer in the vapour was about 2.5 mol%.

4. Structure analysis and results

4.1. Conventional analysis

The least-squares analysis of the experimental molecular intensity curves was performed using a modified version of Seip's program [16]. The theoretical molecular intensity function was calculated according to:

$$sM(s)_t = (1-x) * sM(s)_{\text{monomer}} + x * sM(s)_{\text{dimer}}$$

where x is the relative contribution in the diffraction pattern by dimeric molecules. The parameter x is related to the mole concentration of dimeric molecules χ in the vapour above beryllium dichloride by $x = 2\chi/(1 + \chi)$ [17].

The equilibrium structure of the dimeric molecule Be_2Cl_4 was assumed to have D_{2h} symmetry (see Fig. 3). The independent parameters of the $sM(s)_t$ function were the coefficient x , five parameters of BeCl_2 (two distances $r_a(\text{Be}-\text{Cl})$ and $r_b(\text{Cl}\cdots\text{Cl})$, two root-mean-squares amplitudes $l(\text{Be}-\text{Cl})$ and $l(\text{Cl}\cdots\text{Cl})$, and the anharmonicity parameter $\kappa(\text{Be}-\text{Cl})$) and three parameters for the dimeric molecule ($r_a(\text{Cl}_b\cdots\text{Cl}_t)$, Δ_1 and Δ_2 , where Δ_1 is the difference between the terminal bond length in the dimer $r(\text{Be}-\text{Cl}_t)$ and the bond length $r(\text{Be}-\text{Cl}_a)$ in the monomeric molecule and Δ_2 is the difference between the bridging bond length $r(\text{Be}-\text{Cl}_b)$ in the dimer and the bond length $r(\text{Be}-\text{Cl})$ in the monomeric molecule). The

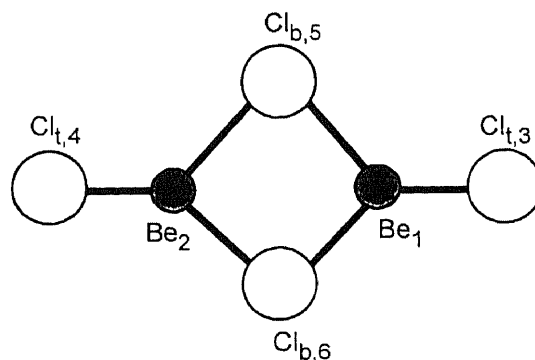


Fig. 3. Molecular model of Be_2Cl_4 (D_{2h} symmetry).

Table 1
Calculated root-mean-squares parallel amplitudes (l_{ij}) and D -corrections for BeCl_2 and Be_2Cl_4 ($T = 547 \text{ K}$)

Parameter	$l_{ij}/\text{\AA}$	D -correction ^a / \AA
BeCl_2		
Be–Cl	0.059	– 0.0125
Cl \cdots Cl	0.076	0.0016
Be_2Cl_4		
Be(1)–Cl _i (3)	0.062	– 0.0436
Be–Cl _b	0.086	– 0.0114
Be \cdots Be	0.106	– 0.0063
Be(1) \cdots Cl _i (4)	0.112	– 0.0143
Cl _i \cdots Cl _i	0.117	0.0018
Cl _i \cdots Cl _b	0.122	– 0.0362
Cl _b \cdots Cl _b	0.100	0.0005

^a D -corrections calculated according to: $D_{ij} = l_{ij}^2/r_{e,ij} - K_{ij}$, where $K_{ij} = (\langle \Delta x_{ij}^2 \rangle + \langle \Delta y_{ij}^2 \rangle)/2r_{e,ij}$ with the mean-square perpendicular amplitudes $\langle \Delta x_{ij}^2 \rangle$ and $\langle \Delta y_{ij}^2 \rangle$.

^b Data for BeCl_2 calculated using spectroscopic frequencies $\nu_2 = 250 \text{ cm}^{-1}$ and $\nu_3 = 1135 \text{ cm}^{-1}$ [6] and assuming $\nu_1 = 373 \text{ cm}^{-1}$ [5].

^c Data for Be_2Cl_4 calculated using frequencies, estimated in present work (see text).

amplitudes (l_{ij}) and D -corrections ($D_{ij} = r_{\alpha,ij} - r_{\alpha}$) were calculated as described below and are given in Table 1. The molecular parameters of Be_2Cl_4 were refined under the constraints of a geometrically consistent r_α structure. The amplitudes (l_{ij}) of the dimer were fixed in the analysis.

The two independent parameters Δ_1 and Δ_2 and the coefficient x were optimized by means of the discrete plans procedure [18] in the intervals 0–0.04 \AA , 0.15–0.22 \AA and 0.0–0.2, respectively. The results of the least-squares analysis are given in Table 2 (second column). The best fit yielded 2.5 mol% ($x = 0.05$) of Be_2Cl_4 . This value agrees well with our data from mass spectral investigation. For comparison, the results of the analysis under the assumption that the vapour consisted of monomeric species only are also listed in this table (first column).

Taking the contribution from the dimeric molecules into account, the agreement between the theoretical and experimental $sM(s)$ curves significantly improves (the R_f value decreases from 5.05 to 4.15%). The structural data for the dimer have low precision because of its small contribution. However, it is

Table 2
Structural parameters for BeCl_2 and Be_2Cl_4 from conventional analysis^a

	r_a^b	r_a	r_g	r_α
BeCl_2				
$r(\text{Be–Cl})/\text{\AA}$	1.801(4)	1.796(4)	1.798(4)	1.783(4)
$r(\text{Cl}\cdots\text{Cl})/\text{\AA}$	3.562(7)	3.565(7)	3.567(7)	3.567(7)
$\angle(\text{Cl–Be–Cl})/\text{deg}$	163(5)	166(5)		180(5)
$l(\text{Be–Cl})/\text{\AA}$	0.060(2)	0.058(2)		
$l(\text{Cl}\cdots\text{Cl})/\text{\AA}$	0.081(2)		0.080(2)	
$\delta_{\text{exp}}(\text{Cl}\cdots\text{Cl})/\text{\AA}$			0.029(15)	
$\delta_{\text{calc}}(\text{Cl}\cdots\text{Cl})/\text{\AA}$			0.030 ^c	
$\kappa(\text{Be–Cl}) \times 10^6/\text{\AA}^3$	10.0(78)	0.0(63)		
Be_2Cl_4				
$r(\text{Be}_1\text{–Cl}_{i,3})/\text{\AA}$	–	1.826(14)	1.828(14)	1.783(14) ^d
$r(\text{Be–Cl}_b)/\text{\AA}$	–	1.964(20)	1.968(20)	1.953(20) ^e
$\angle(\text{Cl}_1\text{–Be–Cl}_b)/\text{deg}$	–	134(4)		135(5)

^a Estimated total errors (σ_i) in parentheses in units of the last significant figures, calculated according to: for distances (r) $\sigma_r = ((\sigma_{\text{sc}})^2 + (2.5\sigma_{\text{LS}})^2)^{1/2}$ and for amplitudes (l) and κ -parameters $\sigma_l = 2.5\sigma_{\text{LS}}$, where σ_{LS} is the least-squares deviation and σ_{sc} is the scale error (0.2%). For bond lengths in the dimer σ_{LS} was calculated according to: $\sigma_{\text{LS}} = ((\sigma_{\text{LS}}(r))^2 + (\sigma_{\text{LS}}(\Delta))^2)^{1/2}$, where $\sigma_{\text{LS}}(r)$ and $\sigma_{\text{LS}}(\Delta)$ are least-squares deviations for r and Δ_1 or Δ_2 , respectively.

^b Results of the analysis under the assumption that the vapor consisted of monomeric molecules only.

^c Calculated using spectroscopic frequency $\nu_2 = 250 \text{ cm}^{-1}$ [6] (see text).

^d Refined value of Δ_1 (difference between $r_\alpha(\text{Be–Cl}_i)$ in the dimer and $r_\alpha(\text{Be–Cl})$ in the monomer) was 0.000(13) \AA .

^e Refined value of Δ_2 (difference between $r_\alpha(\text{Be–Cl}_b)$ in the dimer and $r_\alpha(\text{Be–Cl})$ in the monomer) was 0.17(2) \AA .

important to refine the parameters of Be_2Cl_4 , since the differences between the parameters of the monomer and the corresponding parameters of the dimer are larger than their uncertainties. The further analysis of molecular parameters is based on the results which are given in the second column of Table 2.

The values of thermal-average internuclear distances $r_{g,ij}$ were calculated according to:

$$r_{g,ij} = r_{a,ij} + l_{ij}^2 / r_{a,ij}$$

They are also given in Table 2. The experimental shrinkage value of the $\text{Cl}\cdots\text{Cl}$ distance in BeCl_2 ($\delta_{\text{exp}}(\text{Cl}\cdots\text{Cl}) = 2 * r_g(\text{Be}-\text{Cl}) - r_g(\text{Cl}\cdots\text{Cl}) = 0.029(11)$ Å) agrees well with the value calculated for the linear configuration ($\delta_{\text{calc}}(\text{Cl}\cdots\text{Cl}) = 0.030$ Å, see text below). This confirms the linear equilibrium structure of BeCl_2 .

4.2. Normal coordinate analysis

The values of vibrational amplitudes l_{ij} , D -corrections and the value of shrinkage $\delta(\text{Cl}\cdots\text{Cl})$ at 547 K were calculated for the linear structure of the BeCl_2 molecule on the basis of the vibrational frequencies taken from [6] and assuming $\nu_1 = 373 \text{ cm}^{-1}$ [5]. The formulae which were applied for the calculations were taken from [19]. The values obtained for l_{ij} and D_{ij} are listed in Table 1 and $\delta_{\text{calc}}(\text{Cl}\cdots\text{Cl})$ is given in Table 2.

All frequencies were calculated in [8] for Be_2Cl_4 . However, the values of the force constants have not been published. The authors recommended scaled values of frequencies using an equal scale factor of 0.84 for both bending and stretching frequencies. In our opinion this approach is not valid because the ratios between experimental [6] and calculated [8] frequencies of BeCl_2 are 1.020 and 0.843 for ν_2 and ν_3 , respectively. Therefore, it is necessary to estimate the force constants and frequencies for Be_2Cl_4 .

The dimeric molecule Be_2Cl_4 with D_{2h} symmetry has 12 normal modes of vibrations. However, for only two of them, which correspond to changes of internuclear distances $\text{Be}-\text{Cl}_t$ and $\text{Be}-\text{Cl}_b$, were the frequencies (ν_7 and ν_9) determined experimentally [6,7]. We estimated the force constants and calculated the values of vibrational amplitudes for Be_2Cl_4 using 18 internal vibrational coordinates (see Fig. 4).

The following assumptions and constraints were made for the determination of the force constant values:

1. f_R for $\text{Be}-\text{Cl}_t$ is close to f_r for BeCl_2 ;
2. f_r for $\text{Be}-\text{Cl}_b$ is 2–2.5 times smaller than f_r for BeCl_2 (this ratio is found for force constants of the bridging and terminal bonds for some dimeric molecules of the type M_2X_6 [20]);
3. the values of frequencies $\nu_7(\text{B}_{1u})$ and $\nu_9(\text{B}_{2u})$ calculated on the basis of the force field must be close to the experimental values [4];
4. the bending frequencies calculated on the basis of the force field should not differ very much from the ab initio values [8], because the calculated bending frequency ν_2 for BeCl_2 [8] agrees well with the experimental value [6].

The matrix of force constants consists of nine different constants f_{ij} . They are listed in Tables 3 and 4. The values of the vibrational frequencies were calculated on the basis of these force constants. The starting values f_{ij} were obtained using the geometric parameters of Be_2Cl_4 taken from [8]. On the basis of these f_{ij} values the vibrational amplitudes and D -corrections for Be_2Cl_4 were calculated by means of the program NORCRD [21,22]. After the geometric parameters of Be_2Cl_4 had been refined in a least-squares analysis of $sM(s)$ functions, new geometric parameters were used in the final refinement of the force constants and calculations of the vibrational amplitudes and D -corrections. The resulting values of l_{ij} and D_{ij} are given in Table 1. The values obtained for the force constants and frequencies are given in Tables 3 and 4, respectively.

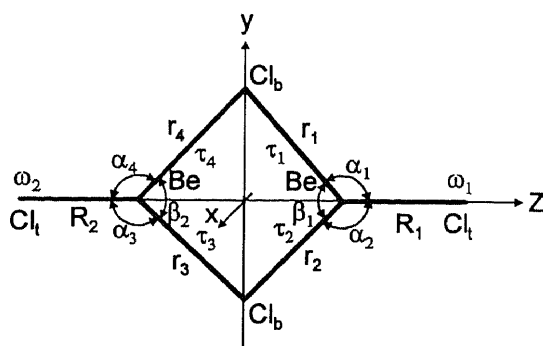


Fig. 4. Internal coordinates for Be_2Cl_4 (D_{2h} symmetry): R, r , stretch; α, β , in-plane bend; ω , out-of-plane bend; τ , torsion.

Table 3
Force Constants (f_{ij}) of Be_2Cl_4 ^a

f_R^b	f_r^b	f_{Rr}^b	f_{rr}^b	$f_{rr'}^c$	f_{α}^c	f_{ω}^c	f_{τ}^c	f_{β}^c
2.84	1.14	0.4	0.15	0.15	0.3	0.2	0.05	0.9

^a For the designation of the internal coordinates see Fig. 4.

^b in mdyn \AA^{-1} .

^c in $\text{mdyn}^2\text{\AA}$.

Our results for the bending frequencies $\nu_3, \nu_4, \nu_6, \nu_{10}, \nu_{11}, \nu_{12}$ are consistent with the ab initio data [8]. The values of the stretching frequencies ν_7 and ν_9 calculated in the present work agree well with the spectroscopic ones [6].

4.3. Analysis of GED data for BeCl_2 in terms of vibrational potential functions

The contribution of the dimer in the experimental $sM(s)$ curve was subtracted. The theoretical $sM(s)_{\text{monomer}}$ curve was described by parameters of different potential functions for a linear molecular structure:

1. Quadratic expression in rectilinear coordinates with the parameters: equilibrium distance r_e^h , stretching force constants f_r and f_{rr} and the bending force constant f_{α} .
2. Quadratic expression in curvilinear coordinates with the parameters: equilibrium distance r_e^{ch} and the force constants f_r, f_{rr} and f_{α} . In this model the

anharmonic effect appears in the kinetic energy part of the vibrational Hamiltonian (kinematic anharmonicity).

3. Cubic expression in curvilinear coordinates with the parameters: equilibrium anharmonic distance r_e^{anh} , the force constants f_r, f_{rr}, f_{α} and the cubic force constant f_{rrr} . In this model the anharmonic effects appear in both the kinetic and the potential energy part of the vibrational Hamiltonian (kinematic and dynamic anharmonicities).

All the models are described in more details elsewhere [23-25] and applied, for example, in [1,26,27]. The least-squares refinement of the vibrational potential function parameters was performed by the method of Hooke and Jeeves [28]. The data obtained for the first potential function model are given in Table 5. The force constant f_{rr} is highly correlated with f_r (correlation coefficient $k(f_r/f_{rr}) = -0.92$), whereas most of the other correlation coefficients are below 0.26.

During the analysis on the basis of the second and third model, f_r and f_{rr} are even more correlated

Table 4
Vibrational frequencies of Be_2Cl_4

	Symmetry coordinates		Frequencies/ cm^{-1}		
			This work	Theor. calc. [8]	Exp. [4]
A_g	$R_1 + R_2$	ν_1	878	965	
	$r_1 + r_2 + r_3 + r_4$	ν_2	352	358	
	$\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4$	ν_3	198	201	
B_{2g}	$\tau_1 + \tau_2 - \tau_3 - \tau_4$	ν_4	256	241	
B_{3g}	$r_1 - r_2 + r_3 - r_4$	ν_5	525	459	
	$\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4$	ν_6	183	175	
B_{1u}	$R_1 - R_2$	ν_7	857	899	
	$\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4$	ν_8	343	303	857
B_{2u}	$r_1 - r_2 - r_3 + r_4$	ν_9	608	636	
	$\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4$	ν_{10}	109	113	608
B_{3u}	$\omega_1 + \omega_2$	ν_{11}	307	316	
	$\tau_1 + \tau_2 + \tau_3 + \tau_4$	ν_{12}	38	34	

Table 5
Parameters of different potential functions for BeCl₂^a

	Quadratic in rectilinear coordinates (model 1)	Quadratic in curvilinear coordinates (model 2)	Cubic in curvilinear coordinates (model 3)	Literature data
Type of distance	r_e^h	r_e^{ch}	r_e^{anh}	
$r(\text{Be-Cl})/\text{\AA}$	1.784(4)	1.796(4)	1.791(5)	1.75(2) ^b
$f_r/\text{mdyn \AA}^{-1}$	3.1(3) ^c	2.8(3)	3.0(3)	
$f_{rr}/\text{mdyn \AA}^{-1}$	-0.5(3)	-0.5 ^d	-0.5 ^d	
$f_{\alpha}/\text{mdyn \AA}^{-1}$	0.075(7)	0.075(7)	0.077(7)	
$f_{rrr}/\text{mdyn \AA}^{-1}$			-2.4(21)	
ν_1/cm^{-1}	353(29) ^e	332(25)	346(29)	
ν_2/cm^{-1}	252(12)	252(12)	256(12)	250 ^f , 482 ^g
ν_3/cm^{-1}	1236(72)	1183(75)	1219(73)	1135 ^f , 1113 ^g

^a Concerning σ_i for distances see footnote a in Table 2; for force constants $\sigma_i = 2.5\sigma_{\text{LS}}$.

^b Obtained by visual technique [2].

^c σ_i for f_r additionally includes uncertainty σ_{scale} which results from the correlation with f_{rr} ; σ_{scale} estimated by varying f_{rr} within its error limits.

^d Fixed value.

^e Uncertainties for frequencies estimated on the basis of uncertainties for force constants.

^f [6].

^g [4].

($k(f_r/f_{rr}) = -0.96$). Therefore, f_{rr} was fixed at the value $-0.5 \text{ mdyn \AA}^{-1}$, which was obtained for the first model. The results are also given in Table 5. In the case of the anharmonic analysis r_e^{anh} and f_{rrr} also highly correlate ($k(r_e^{\text{anh}}/f_{rrr}) = 0.96$) and consequently their errors are large (see Table 5).

The Morse constant can be estimated according to [29]: $a = -2f_{rrr}/(f_r * r_e^{\text{anh}})$. The calculated value is equal to $0.9(8) \text{ \AA}^{-1}$.

5. Discussion

Two molecular species BeCl₂ and Be₂Cl₄ were detected in the saturated vapour over solid beryllium dichloride at 547 K with the ratio 97.5 to 2.5 mol%. Our conclusions agree well with Hildenbrand's data [9], obtained under similar conditions, and disagree with the results of Ko et al. [11], which have large uncertainties.

The values of r_{α} and r_e^h obtained for the Be-Cl distance in the linear molecule BeCl₂ are practically equal. This is not surprising because in both cases the vibrational corrections were calculated in rectilinear coordinates using a harmonic approximation.

The contribution by the kinematic anharmonicity

(Δ_{kin}) to the internuclear distance may be estimated as the difference between r_e^h and r_e^{ch} values. The resulting $\Delta_{\text{kin}} = -0.012 \text{ \AA}$ exceeds the sum of error limits of these parameters. The contribution by the dynamic anharmonicity (Δ_{dyn}) may be estimated as the difference between r_e^{ch} and r_e^{anh} . The value obtained, $\Delta_{\text{dyn}} = 0.005 \text{ \AA}$, is within the error limits of the distances. Therefore, it is more important to take into account the kinematic anharmonicity than the dynamic one. That means that the r_e^{ch} and the practically equal r_g values are better estimates of the molecular distance Be-Cl than the r_e^h and r_{α} values, respectively. However, in our opinion the r_e^{anh} value is the best estimate of the equilibrium distance, despite the greater error.

Small values of the Morse constant and the anharmonicity parameter $\kappa(\text{Be-Cl})$ in the conventional analysis also reflect the small dynamic anharmonicity for BeCl₂.

Our data for the frequencies $\nu_2 = 256(12) \text{ cm}^{-1}$ and $\nu_3 = 1219(73) \text{ cm}^{-1}$ agree well with the spectroscopic data by Snelson (250 and 1135 cm^{-1} , respectively [6,7]) and disagree with Klemperer's data [4] for ν_2 (482 cm^{-1}). Our result for ν_1 ($346(29) \text{ cm}^{-1}$) is consistent with the value estimated by Baikov (373 cm^{-1} [5]).

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