

Equilibrium structure of beryllium difluoride from least-squares analysis of gas-phase electron diffraction data[☆]

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Abstract

The molecular structure of beryllium difluoride has been studied by means of gas-phase electron diffraction. The thermal average (r_g) bond length Be–F at 758°C is 1.386(3) Å. The equilibrium structure is linear with the bond length 1.374(4) Å. Force constants and vibrational frequencies have been obtained from gas-phase electron diffraction data alone.

1. Introduction

The present work is a continuation of our systematic investigations of metal difluorides by means of gas-phase electron diffraction (GED) [1–5]. The high-temperature evaporation (up to 1500 K) of these substances and the high reactivity of these vapours create various experimental problems. The large-amplitude vibrations in the molecules, which are coupled with the high-temperature conditions, make the analysis of the electron diffraction data complicated. Moreover, for beryllium difluoride precise measurements are even more difficult because of the weak scattering properties.

Experimental structural data for beryllium difluoride were first obtained in 1957 by Akishin and Spiridonov [6] by means of the visual GED method, which gave $r(\text{Be–F}) = 1.40(3)$ Å and

$\angle(\text{F–Be–F}) = 180(30)^\circ$ in low precision by modern standards. Büchler et al. [7] confirmed the linear structure, since they failed to observe the refocussing of the molecular beam in an electric field. In a further study, Büchler and Klemperer [8] investigated the low-resolution gas-phase infrared spectrum and assigned the bands at 825 and 1520 cm^{−1} to the vibrational frequencies ν_2 and ν_3 , respectively. However, according to the matrix infrared data of Snelson [9], which were corrected for matrix shifts, ν_2 and ν_3 were 345 and 1555 cm^{−1}, respectively. Snelson [9] suggested a linear configuration of the molecule because the symmetrical stretching mode ν_1 was not detected in the spectrum. The value of ν_1 was estimated to be 680 cm^{−1} using a simple valence force field approximation. Snelson's value for ν_3 agrees exactly with the gas-phase value of Frum et al. [10] obtained from the high-resolution infrared emission spectrum. From the rotational and rotation–vibration interaction constants, the equilibrium distance $r_e(\text{Be–F})$ was determined to be 1.3729710(95) Å

[☆] Dedicated to Professor Yonezo Morino on his 87th birthday.

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[10]. The Raman spectrum of beryllium difluoride is not known. *Ab initio* studies [11–15] predict a linear configuration for beryllium difluoride with $r_e(\text{Be-F})$ in the broad interval between 1.36 and 1.43 Å. The theoretical values for ν_3 are systematically higher (up to 15%) than the spectroscopic ones.

In this work we present the results of the structural GED analysis of beryllium difluoride.

2. Experimental

Beryllium difluoride was prepared by slowly heating ammonium tetrafluoroberyllate to 550°C according to the method described by Rakov and Melnichenko [16]. The ammonium tetrafluoroberyllate was synthesised by dissolving beryllium metal in an aqueous solution of ammonium fluoride. Mass spectrometric analysis of the resulting BeF_2 sample, using the monopole mass spectrometer APDM-1 [17], showed no measurable volatile by-product up to 800°C.

The electron diffraction pattern was obtained by a modified EMR-100 instrument [18] at an accelerating voltage of 73 keV for the nozzle-to-plate distances $L_1 = 598$ mm and $L_2 = 338$ mm (four plates each). The sample was vaporised from a nickel cell at 758°C. The simultaneous measurement of the mass spectrum showed that monomeric BeF_2 is the only species in the vapour; the

relative intensities were 43, 100, and 2.4 for the ion peaks of BeF_2^+ , BeF^+ , and Be^+ , respectively. The dimer ions were absent at a level of about 0.5%.

3. Structure analysis and results

3.1. Conventional analysis

The molecular intensity curves are shown in Fig. 1. The electron scattering factors were taken from tables [19]. The two peaks in the radial distribution curve (Fig. 2) can be assigned to the Be–F and F···F distances. The final results of the conventional analysis (bond lengths r_a , root-mean-squares parallel amplitudes l , and the anharmonicity parameter κ) are listed in Table 1. The correlation coefficients k for the refined parameters were below 0.25 except $k(r/\kappa) = 0.81$ for the Be–F term.

The thermal average bond length r_g was calculated according to the equation (see, for example, [20,21]): $r_g \approx r_a + l^2/r_a$.

3.2. Analysis in terms of vibrational potential functions

Two vibrational potential function models were applied to determine the equilibrium structure.

(1) A semirigid model in curvilinear coordinates with harmonic stretching and anharmonic bending potential functions [22]. The bending potential has

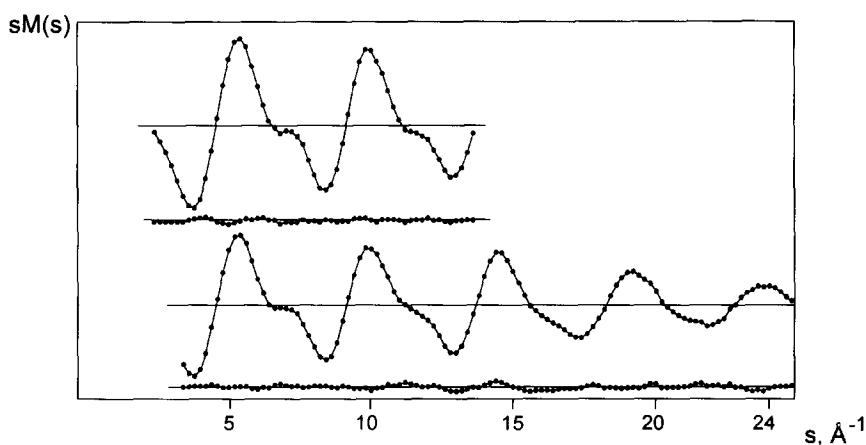
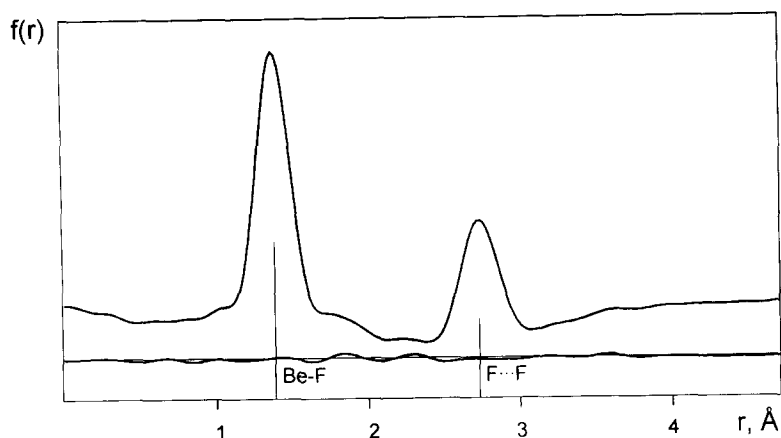


Fig. 1. Experimental molecular intensity curves and corresponding difference curves (experimental – theoretical) for BeF_2 at two nozzle-to-plate distances ($L_1 = 598$ mm for the upper pair of traces, $L_2 = 338$ mm for the lower pair of traces).

Fig. 2. Experimental radial distribution curve and difference curve for BeF₂.

the form $V = \frac{1}{2} k_2 \rho^2 + k_4 \rho^4$, where k_2 and k_4 are the quadratic and quartic force constants, $\rho = \pi - \alpha$ is a variable with the bond angle α in radians, and describes linear as well as bent equilibrium configurations. Molecules are linear if k_2 is positive ($\rho_e = 0$) or bent if k_2 is negative (although k_4 is positive). In the case of linear molecules the force constants f_r , f_{rr} , k_2 and k_4 may be refined in the least-squares analysis.

The refinement of the vibrational potential function parameters was performed by the method of Hooke and Jeeves [23]. Because of the strong correlation with f_r , the force constant f_{rr} was constrained to several values in the interval from -0.5 to $+0.5$ mdyn Å⁻¹. Different assumptions for f_{rr} do

not significantly change the R factors and the refined parameters except f_r , which varies by 0.2 mdyn Å⁻¹. This variation was taken into account to estimate the uncertainty of f_r . Finally $f_{rr} = -0.5$ mdyn Å⁻¹ was used as constraint in the following analysis.

The optimised parameters are listed in Table 2. The correlation coefficients are: $k(r/f_r) = 0.22$, $k(r/k_2) = -0.72$, $k(r/k_4) = 0.72$, $k(f_r/k_2) = -0.37$, $k(f_r/k_4) = 0.38$, and $k(k_2/k_4) = -0.99$. The positive value of the quadratic force constant k_2 proves the linearity of the equilibrium configuration for the BeF₂ molecule. The effect of the dynamic anharmonicity of the deformation vibration is small ($k_4 \approx 0$).

Vibrational frequencies, calculated from the force constants, are given in Table 3. The calculation of

Table 1
Structural parameters of BeF₂ at 758°C from conventional GED analysis^{a,b}

	Be-F	F...F
r_a (Å)	1.384(3) ^c	2.733(6) ^c
l (Å)	0.062(2)	0.092(3)
$10^6 \kappa$ (Å ³)	3(6)	[0] ^d
r_g (Å)	1.386(3)	2.736(6)

^a Estimated total error in parentheses in units of the last significant figures, calculated according to $\sigma_t = [4\sigma_{LS}^2 + \sigma_{sc}^2]^{1/2}$, where σ_{LS} is the least-squares deviation and σ_{sc} the scale error were taken to be 0.2, 2 and 20% for distances (r), amplitudes (l), and anharmonicity parameters (κ), respectively.

^b $R_f(L_1) = 3.4\%$ and $R_f(L_2) = 6.8\%$.

^c Corresponding $\angle_a(\text{F}-\text{Be}-\text{F}) = 162(6)^\circ$.

^d Assumed.

Table 2
Force constants of BeF₂ from GED data^a

		Potential function models	
		Semirigid	Cubic
f_r	(mdyn Å ⁻¹)	4.45(60)	4.20(60)
f_α	(mdyn Å ⁻¹)		0.15(2)
f_{rr}	(mdyn Å ⁻¹)		-4.6(22)
k_2	(mdyn Å)	0.26(26)	
k_4	(mdyn Å)	0.02(38)	
$R_f(L_1)$	(%)	3.4	3.8
$R_f(L_2)$	(%)	6.8	7.0

^a 2σ as uncertainties, for f_r additional error taken into account due to the assumption of $f_{rr} = -0.5$ mdyn Å⁻¹ (see text).

Table 3
Molecular constants of BeF₂

	This work	Literature data
r_e (Å)	1.374(4) ^a	1.3729710(95) ^d
a (Å ⁻¹)	1.6(8) ^b	
$\omega_{e2}x_e$ (cm ⁻¹)	-1.0	
ω_{e2} (cm ⁻¹)	352	
ν_1 (cm ⁻¹)	594(60) ^c	
ν_2 (cm ⁻¹)	354(27)	345 ^e , 825 ^f
ν_3 (cm ⁻¹)	1519(90)	1555 ^{e,g} , 1520 ^f

^a See footnote a in Table 1.

^b Morse constant calculated according to $a = -2f_{rr}/(f_r \times r_e)$ [26].

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

^d Calculated from high-resolution infrared data, uncertainty one standard deviation [10].

^e Ref. [9].

^f Ref. [8].

^g Ref. [10].

the deformation vibrational spectrum was performed by numerical integration of the Schrödinger equation with Hamiltonian (8) in Ref. [22] with the aid of the Numerov–Cooley procedure [24]. The resulting value of the harmonic spectroscopic constant ω_{e2} is also listed in Table 3. The corresponding anharmonicity constant $\omega_{e2}x_e = -1.0 \text{ cm}^{-1}$ is much smaller than the estimated error of ν_2 . That means that the influence of the kinematic and dynamic anharmonic effects on the frequencies of the transitions is negligibly small. This conclusion is consistent with the results of ab initio calculations [13].

(2) A simple anharmonic model in curvilinear coordinates, in which only cubic terms are considered [25,26]; the application of this model has been shown for example in Ref. [27]. The anharmonic effects are taken into account in both the kinetic and potential energy part of the Hamiltonian. The limitation by the cubic constant f_{rrr} leads to an optimal number of refined parameters. The equilibrium distance Be–F, which characterises the potential minimum, is called here r_e . For linear molecules the force constants f_r , f_{rr} , f_α and f_{rrr} may be refined in the least-squares analysis. The method and details of the optimisation are described above.

The final values of the force constants are listed in Table 2, whereas the equilibrium distance r_e is

Table 4
Different types of internuclear distances $r(\text{Be–F})^a$

Type	Value (Å)
r_a	1.384(3)
r_g	1.386(3)
r_c	1.374(4)
r	1.40(3) ^b
r_e	1.3729710(95) ^c

^a Uncertainties for r in this work estimated as specified in footnote a in Table 1.

^b Visual GED method, structure type not specified [6].

^c Ref. [10], see footnote d in Table 3.

given in Table 3. The correlation coefficients between the parameters of anharmonic potential are less than 0.22 except $k(r/f_{rrr}) = 0.95$.

4. Conclusions

Values for the internuclear distance Be–F, obtained by different methods, are presented in Table 4. The good agreement of the resulting equilibrium bond length r_e with recent high-resolution infrared data may demonstrate for special cases the reliability of the determination of equilibrium structure from GED data alone. The difference between r_g and r_e of 0.012 Å is significantly larger than the error limits. That means that the vibrational corrections in the GED analysis may be very useful for the determination of the molecular geometry. For BeF₂ they can be performed with sufficient accuracy in curvilinear coordinates and by the consideration of the dynamic anharmonicity of the stretching vibrations. The resulting r_e value is also suitable for testing the results of ab initio calculations.

The resulting frequency $\nu_2 = 354 \text{ cm}^{-1}$ confirms Snelson's spectroscopic value (345 cm^{-1}). This band could not be observed by Büchler and Klemperer [8], because they measured the vibrational spectrum in the limited spectral range 2300–700 cm^{-1} . Obviously the weak band at 825 cm^{-1} was misassigned. The obtained frequency $\nu_3 = 1519 \text{ cm}^{-1}$ and the corresponding force constant in symmetry coordinates $F_3 = f_r - f_{rr} = 4.95 \text{ mdyn Å}^{-1}$ agree well with spectroscopic data

($\nu_3 = 1555 \text{ cm}^{-1}$ and $F_3 = 5.15 \text{ mdyn Å}^{-1}$). Our result for ν_1 is consistent with the estimated values 670 [28] and 680 cm^{-1} [9], but is characterised by a relatively large error. The measurement of the Raman spectrum is desirable.

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