Fourier transform emission spectroscopy of BeF$_2$ at 6.5 µm

C. I. Frum, R. Engleman, Jr., and P. F. Bernath

Department of Chemistry, The University of Arizona, Tucson, Arizona 85721

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The high resolution infrared emission spectrum of BeF$_2$ was observed. The fundamental antisymmetric stretching mode $v_2$ and numerous hot bands involving $v_1$ and $v_3$ were found near 1550 cm$^{-1}$ by Fourier transform spectroscopy. Eight vibration-rotation bands were rotationally analyzed and the spectroscopic constants are reported. The equilibrium beryllium fluorine distance ($r_e$) was found to be 1.372 9710(95) Å in BeF$_2$.

I. INTRODUCTION

A considerable body of work exists on the subject of the geometry of triatomic metal dihalide molecules. The available experimental data includes electron diffraction, photoelectron spectra, matrix isolation studies, and low resolution gas-phase spectroscopy. In spite of this work, the question of linear versus bent geometries remains to be definitively answered for many molecules. Recently, there has been a revival in the theoretical interest in this area. The problem is that no high resolution, rotationally resolved spectra are available. Some progress has been made by jet-cooling metal dihalides such as NiCl$_2$ and recording electronic transitions by dye laser spectroscopy. We report here the first complete rotational analysis of the spectrum of a metal dihalide molecule.

The structure and bonding in metal halide molecules has been of great interest to both experimentalists and theoreticians. The experimental work on alkaline earth dihalides started in the 1950’s with the observation of electron diffraction by Akishin, Spiridonov and co-workers. They concluded that all of the alkaline earth dihalide molecules have linear geometries although the determination of the X-M-X angle was subject to a large error ($\pm$ 30°-40°).

Klemperer and co-workers studied the molecular geometry of high temperature molecules by the deflection of molecular beams by electric fields. The refracting of a beam of polar molecules by an electric quadrupole was detected with a surface ionization detector or a mass spectrometer. Surprisingly, all of the barium dihalides, SrF$_2$, SrCl$_2$, and CaF$_2$, were found to have a dipole moment as expected for bent molecules of C$_2v$ symmetry. It was noted that the symmetrical alkaline earth dihalides become bent as the central metal atom becomes heavier and as the halogen atoms become more electronegative.

The observation of infrared and Raman spectra of matrix isolated alkaline earth dihalides confirmed the deflection results of Klemperer and co-workers, although MgF$_2$ was briefly controversial. The more recent electron diffraction data are consistent with conclusions of Klemperer and co-workers. Photoelectron spectra are also available for some of the alkaline earth dihalides.

Büchler and Klemperer observed the low resolution gas-phase infrared absorption spectrum of hot BeF$_2$. They found the vibrational frequencies, $v_2$ and $v_3$, to be 825 and 1520 cm$^{-1}$, respectively. The definitive low resolution analysis, however, was the matrix isolation work of Snelson. Snelson determined $v_2$ and $v_3$ to be 345 and 1555 cm$^{-1}$ for BeF$_2$, empirically correcting for matrix shifts. Remarkably, Snelson’s value for $v_2$ agrees exactly with the gas-phase value determined in our work. The $v_2$ value of Snelson is also undoubtedly correct and, indeed, we find no evidence for $v_2$ above 300 cm$^{-1}$ in our high resolution spectra.

The alkaline earth dihalides are mainly monomeric in the gas phase, although dimers and higher aggregates are present. Mass spectrometric studies are generally consistent with dimer concentrations of 1%-2% and matrix isolation work on the dimers is available.

The alkaline earth dihalides have been the subject of numerous theoretical papers, partly because they violate simple bonding rules. For example, both the valence electron pair repulsion (VSEPR) “theory” and Walsh’s rules predict linear geometries for the alkaline earth dihalides.

Two general physical models are used to rationalize bent structures. The participation of $d$ orbitals on the alkaline earth ions favors nonlinear geometries as does strong polarization of the alkaline earth ion by anions. Although these simple models are physically appealing, they both have been heavily criticized. The Rittner-type ionic models are particularly vulnerable because they use “arbitrary” values of the polarizabilities.

II. EXPERIMENTAL

The high resolution infrared emission spectrum of BeF$_2$ was observed with the National Solar Observatory Fourier transform spectrometer at Kitt Peak. The unpolarized resolution was 0.0055 cm$^{-1}$ with liquid helium cooled As:Si detectors and a KCl beam splitter. The spectral bandpass was limited to 500-2900 cm$^{-1}$ with a wedged InAs filter placed at the entrance aperture of the instrument. The upper wave number limit was set by this filter while the lower limit was determined by the transmission of the KCl beam splitter and by the detector response.

Gas-phase BeF$_2$ was produced in an alumina tube furnace by heating solid BeF$_2$ to a maximum temperature of...
about 1000 °C. The apparatus used was described previously in our observation of emission spectrum of SiS. The deposition of solid material onto the windows was avoided by pressurizing the system with 5 Torr of Ar. The temperature of the furnace, as measured by a chromel-alumel thermocouple placed between the heating elements and the ceramic tube, was increased at a steady rate of about 2 °C/min. A series of spectra were recorded as the cell heated up and then cooled down. Initially we placed a glover behind the cell and focused its image on the 8 mm aperture of the instrument to look for absorption spectra. No absorption was observed, but when the glover was shut off, strong emission spectra of BeF₂ were recorded. As the furnace cooled down from 1000 °C, the intensity of the emission signal decreased rapidly and disappeared at about 500 °C. The best spectrum (with the least amount of congestion) was obtained at about 700 °C. Spectra recorded at lower temperatures were too weak, while higher temperature spectra exhibit line intensity anomalies as well as stronger hot bands. The intensity anomalies seen, for example, near the band heads shown in Fig. 1, seem to be associated with the changing temperature and pressure during the scan integration. As the temperature dropped, a series of spectra were recorded by co-adding three scans in fifteen minute integration intervals.

III. RESULTS AND ANALYSIS

PC-DECOMP, a spectral analysis program developed by J. W. Brault of the National Solar Observatory, was used for data analysis. The rotational profiles were fitted to Voigt line shape functions. Although the spectrum shows considerable congestion due to the overlap of numerous hot bands, the line density is much lower at the blue end of the region where the fundamental band makes an R head (Fig. 1). These strong sharp lines show “ringing” caused by the sin x/x instrument line shape function of the Fourier transform spectrometer. The ringing was eliminated by using the “filter fitting” routine available in PC-DECOMP. The filter fit option also provided some degree of resolution enhancement. For the strong lines of BeF₂ (Figs. 1 and 2), the signal-to-noise ratio was better than 120 and the resulting resolution-enhanced linewidth was 0.002 cm⁻¹. The precision of strong, unblended lines is better than 0.0001 cm⁻¹, but the presence of numerous overlapping lines (Fig. 2) degrades this. The absolute calibration (± 0.0002 cm⁻¹) was provided by impurity H₂O vapor absorption inside the cell.

In the antisymmetric stretch region we were able to identify 24 infrared bands and we assigned eight: the fundamental transition and seven hot bands. The bands were picked out using an interactive color Loomis-Wood program which runs on a 386/25 microcomputer. An energy level diagram indicating the assigned transitions is shown in Fig. 3.

The antisymmetric stretching fundamental, ν₃, 001–000, S_u⁺–S_g⁺, was easy to identify because it was the strongest band in this region. In addition, the high-JR branch of this band was free of overlap. The hot bands, due to vibrational anharmonicity, are shifted to the red. Because of the high temperature all of the bands display prominent R heads (Fig. 1).

More than 200 rotational lines of the fundamental ν₃ transition, 128 in the P branch and 91 in the R branch, were measured. The weak R(0) and P(1) lines were also found, but they were heavily blended with other lines (Fig. 2). The absolute rotational assignment of each band was difficult because of the high density of overlapping lines in the origin regions. Nuclear spin statistics caused by the equivalent fluorine nuclei (I = 1/2) produces a 3:1 intensity alternation (Fig. 1) and constrains the rotational assignment. For each band, various absolute rotational assignments were considered and the final assignments were made by comparison with the analogous spectrum of the isoelectronic molecule, CO₂. Fortunately, the key assignment for the fundamental band could be made on the basis of the “missing line” at the band origin (Fig. 2).

The absolute rotational assignment of the hot bands was considerably harder than for the fundamental band. The following hot bands were assigned:

<table>
<thead>
<tr>
<th>J₁</th>
<th>J₂</th>
<th>Δν₂</th>
<th>Δν₃</th>
<th>Δν₄</th>
<th>Δν₅</th>
<th>Δν₆</th>
</tr>
</thead>
<tbody>
<tr>
<td>01</td>
<td>01</td>
<td>00</td>
<td>00</td>
<td>00</td>
<td>00</td>
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</tr>
<tr>
<td>02</td>
<td>02</td>
<td>00</td>
<td>00</td>
<td>00</td>
<td>00</td>
<td>00</td>
</tr>
<tr>
<td>03</td>
<td>03</td>
<td>00</td>
<td>00</td>
<td>00</td>
<td>00</td>
<td>00</td>
</tr>
</tbody>
</table>

FIG. 1. Infrared emission spectrum of BeF₂ in the region of the antisymmetric stretching mode ν₃. All of the vibrational bands make R heads at high J values. The intensity alternation due to fluorine nuclear spin statistics can be clearly seen in the fundamental band.
the \( \Sigma \rightarrow \Sigma \) Fermi dyad,
\[
02^{+}1-02^{+}0, \quad \Sigma_{v}^{+}-\Sigma_{u}^{+},
101-100, \quad \Sigma_{v}^{+}-\Sigma_{u}^{+},
\]
and the \( \Pi \rightarrow \Pi \) Fermi dyad,
\[
03'1-03'0, \quad \Pi_{v}-\Pi_{u},
11'1-11'0, \quad \Pi_{v}-\Pi_{u}.
\]
The \( 01'1-01'0, \ \Pi_{v}-\Pi_{u} \) band was the strongest hot band. Although the band origin was very congested, we were able to obtain an absolute rotational assignment because the variance of the fit showed a clear minimum for the correct assignment. The other two \( \Pi_{v}-\Pi_{u} \) transitions of the \( \Pi \rightarrow \Pi \) Fermi dyad also were assigned in this way although the data were relatively poor for these two bands. The sign of the \( l \)-type doubling constant \( q \) was determined by comparison with the corresponding transitions in \( \text{CO}_{2} \).

The \( 02^{+}1-02^{+}0, \ \Delta_{v}-\Delta_{u} \) band shows \( l \)-type resonance splitting only at very high \( J \) values. The absolute rotational assignment for this band was made by using the \( \alpha_{v} \) value (Table II) obtained from the \( 001-000 \) and the \( 01'1-01'0 \) bands. The correct rotational assignment of the \( \Delta_{v}-\Delta_{u} \) band also showed a minimum in the variance of the fit. The \( 03'1-03'0, \ \Phi_{v}-\Phi_{u} \) band was assigned in a similar fashion but, as expected, no \( l \)-type splittings were observed.

The most difficult bands to assign were the two \( \Sigma_{v}^{+}-\Sigma_{u}^{+} \).
bands (02°1-02°0, 101-100) in the Σ–Σ Fermi dyad. The strong Fermi interaction perturbs the \( B \) values so that, for example, \( B_{02°0} \neq B_{02°1} \). The comparison with CO, again proved to be indispensable in guiding our assignments.

The \( B_{02°0} \) value was shifted down by 0.000 943 cm\(^{-1}\) by the mixing of the 02°0 and 100 vibrational wave functions. The molecular constants for the observed BeF, bands are provided in Table I. The line positions are available through PAPS or directly from the authors.

In the fitting and labeling of our data we have followed the conventions of electronic spectroscopy. We used the simple rotational energy expression:

\[
F(J) = BJ(J+1) - D[J(J+1)]^2 + \frac{J(J+1)}{2}
\times [q + q_D(J+1)],
\]

where \( q = q_D = 0 \) for Σ states; \( q = 0 \) for Δ states and the upper (lower) sign refers to \( \sigma(\pi) \) parity. The \( \ell \)-type doubling parameter \( q \) is negative in 010 vibrational state because the \( \pi \) parity level lies above the \( \sigma \) parity level for a given \( J \). This arbitrary choice is in agreement with the conventions of electronic spectroscopy but differs from the commonly used infrared convention of a positive sign for \( q \). The recent work on the corresponding spectra of CO, by Bailly and co-workers uses a negative sign for \( q \).

In addition to the bands observed near 1550 cm\(^{-1}\) some very weak \( Q \) branches were found in the region 1127-1235 cm\(^{-1}\). These bands are probably associated with the \( \nu_1 + \nu_2 \) combination band (11°0-000) of \( \Pi_{\pi} - \Sigma_{\pi}^+ \) symmetry. If this assignment is correct, then the value for \( \nu_1 \) lies between 780 and 890 cm\(^{-1}\). This value is somewhat higher than the value of 680 cm\(^{-1}\) estimated from the \( \nu_1 \) band using the valence force approximation. A gas-phase Raman measurement of \( \nu_1 \) for BeF, is desirable.

### IV. DISCUSSION

The geometry of BeF, can be extracted from the molecular constants provided in Table I. The \( r_0 \) Be–F bond distance of 1.374 040 3 Å is found using the \( B_{010} \) value. Since bands involving all three normal modes were found, it is possible to determine \( B_{010} \) as well as \( \alpha_1, \alpha_2, \) and \( \alpha_3: \)

\[
B_{010} = B_{010} - \alpha_1 (\nu_1 + \frac{1}{2}) - \alpha_2 (\nu_2 + 1) - \alpha_3 (\nu + \frac{1}{2}).
\]

The \( \alpha_2 \) and \( \alpha_3 \) values (Table II) were found by using the \( B_{010}, B_{001}, \) and \( B_{000} \) values of Table I. The observed \( \alpha_1 \) value of -0.000 148 6(103) cm\(^{-1}\) was corrected for the effects of Fermi resonance by using the observed \( B_{02°0} - B_{02°1} \) shift to provide an \( \alpha_1 \) (corrected) = 0.000 794 3(52) cm\(^{-1}\). The \( B_{010} \) of Table II results in a \( r_e \) of 1.372 971 0(95) Å where the quoted one standard deviation uncertainty is a simple statistical error estimate.

The electron diffraction measurement for BeF, provides a Be–F bond distance of 1.40 ± 0.03 Å. The observed \( r_e \) value is also in good agreement with the \( r_e \) of 1.380 Å recently calculated by Dyke and Wright, as well as the previous \textit{ab initio} calculations. For the diatomic BeF molecule \( r_e \) is 1.3610 Å, very close to the 1.3730 Å value found in BeF,.

The unpaired electron in the \( X^2 \Sigma^+ \) ground state of BeF is clearly nonbonding.

### TABLE I. Molecular constants for BeF,.

<table>
<thead>
<tr>
<th>Level</th>
<th>Band* origin</th>
<th>( B_{010}, \nu_2, \nu_3 )</th>
<th>( 10^5 D_{010}, \nu_2, \nu_3 )</th>
<th>( 10^5 q_1 )</th>
<th>( 10^5 q_D )</th>
</tr>
</thead>
<tbody>
<tr>
<td>00°0</td>
<td>1555.047 92(5)</td>
<td>0.234 990 66(56)</td>
<td>0.101 680(47)</td>
<td>0.091 04(9)</td>
<td>0.07(11)</td>
</tr>
<tr>
<td>00°1</td>
<td>01°0</td>
<td>0.232 544 62(57)</td>
<td>0.100 878(49)</td>
<td>0.106 464(76)</td>
<td></td>
</tr>
<tr>
<td>01°1</td>
<td>02°0</td>
<td>0.236 69(66)</td>
<td>0.105 732(78)</td>
<td>0.111 050(84)</td>
<td></td>
</tr>
<tr>
<td>02°1</td>
<td>03°0</td>
<td>0.233 816 87(66)</td>
<td>0.105 732(78)</td>
<td>0.111 050(84)</td>
<td></td>
</tr>
<tr>
<td>03°1</td>
<td>1553.465 82(7)</td>
<td>0.236 732 02(70)</td>
<td>0.110 354(87)</td>
<td>0.115 750(62)</td>
<td></td>
</tr>
<tr>
<td>10°0</td>
<td>1543.272 14(8)</td>
<td>0.236 342 15(71)</td>
<td>0.115 059(65)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10°1</td>
<td>02°0</td>
<td>0.236 139 26(87)</td>
<td>0.083 689(80)</td>
<td>0.093 55(76)</td>
<td></td>
</tr>
<tr>
<td>02°1</td>
<td>1542.340 80(92)</td>
<td>0.236 549 71(97)</td>
<td>0.083 049(84)</td>
<td>0.127 254(83)</td>
<td></td>
</tr>
<tr>
<td>11°0</td>
<td>1535.782 31(7)</td>
<td>0.236 428 72(91)</td>
<td>0.092 50(11)</td>
<td>0.051 4(10)</td>
<td></td>
</tr>
<tr>
<td>11°1</td>
<td>03°0</td>
<td>0.237 978 23(92)</td>
<td>0.091 51(12)</td>
<td>0.331 3(10)</td>
<td>0.582 47(64)</td>
</tr>
<tr>
<td>03°1</td>
<td>1535.503 97(6)</td>
<td>0.237 693 22(84)</td>
<td>0.125 122(90)</td>
<td>0.124 554(83)</td>
<td></td>
</tr>
</tbody>
</table>

*One standard deviation error is enclosed in parentheses.

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The II vibrational levels show $\ell$-type doubling splittings and the $\Delta$ vibrational levels display $\ell$-resonance splittings as expected for transitions associated with doubly degenerate modes. For a symmetric linear triatomic molecule, the magnitude of the splitting is given by the equation:

$$\Delta \nu = qJ(J + 1) + q_D[J(J + 1)]^2 + \cdots$$

For vibrational states of $\Delta$ symmetry, $q = 0$ and the leading term is $q_D$. For a linear, symmetric triatomic molecule such as $\text{BeF}_2$, the value of $q$ is given by:

$$q = -\frac{B_2^2}{\omega_2} \left(1 + \frac{4\omega_2^2}{\omega_3^2 - \omega_2^2}\right)(v_2 + 1).$$

Using $\omega_{00} = -0.3874(13)$ cm$^{-1}$, $B_{00} = 0.23499$ cm$^{-1}$ and $v_2 = 1555$ cm$^{-1}$, Eq. (2) predicts $v_2 = 345$ cm$^{-1}$ in remarkable agreement with Snelson's value of 345 cm$^{-1}$.

The detailed theory of $I$-resonance in $A$ states was first derived by Amat and Nielsen with later contributions by Maki and Lide. The sign of $q_D$ indicates that the $02_{00}$ vibrational level lies higher in energy than the $02_{02}$ level. In addition the changes in the centrifugal distortion constants relative to the ground state are consistent with the 102 vibrational level lying above the 020 level.

V. CONCLUSION

The high resolution infrared emission spectrum of $\text{BeF}_2$ vapor at 700°C was observed with a Fourier transform spectrometer. The antisymmetric stretching mode $\nu_1$ near 1555 cm$^{-1}$ and seven hot bands were rotationally analyzed. From the equilibrium rotational constant, the equilibrium $\text{Be}-\text{F}$ bond distance of 1.372917(95) Å was calculated for $\text{BeF}_2$. Our work represents the first complete rotational analysis of a metal dihalide. The rather neglected technique of high resolution infrared emission spectroscopy promises to be a powerful tool for the determination of molecular structures of high temperature molecules.

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