

Fourier transform emission spectroscopy of BeF₂ at 6.5 μm

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The high resolution infrared emission spectrum of BeF₂ was observed. The fundamental antisymmetric stretching mode ν_3 and numerous hot bands involving ν_1 and ν_2 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 BeF₂.

I. INTRODUCTION

A considerable body of work exists on the subject of the geometry of triatomic metal dihalide molecules.¹ 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.² Recently, there has been a revival in the theoretical interest in this area.³⁻⁹ The problem is that no high resolution, rotationally resolved spectra are available. Some progress has been made by jet-cooling metal dihalides such as NiCl₂ and recording electronic transitions by dye laser spectroscopy.¹⁰ 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 dihalide molecules started in the 1950's with the observation of electron diffraction by Akishin, Spiridonov and co-workers.¹¹ 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 ($\pm 30^\circ$ - 40°).

Klemperer and co-workers¹²⁻¹⁴ studied the molecular geometry of high temperature molecules by the deflection of molecular beams by electric fields. The refocusing of a beam of polar molecules by an electric quadrupole was detected with a surface ionization detector or a mass spectrometer.¹²⁻¹⁵ Surprisingly, all of the barium dihalides, SrF₂, SrCl₂, and CaF₂, 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 dihalides¹⁶⁻³⁰ confirmed the deflection results of Klemperer and co-workers, although MgF₂ was briefly controversial.³⁰ The more recent electron diffraction data³¹⁻³⁴ are consistent with conclusions of Klemperer and co-workers. Photoelectron spectra^{35,36} are also available for some of the alkaline earth dihalides.

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Büchler and Klemperer²⁷ observed the low resolution gas-phase infrared absorption spectrum of hot BeF₂. They found the vibrational frequencies, ν_2 and ν_3 to be 825 and 1520 cm⁻¹, respectively. The definitive low resolution analysis, however, was the matrix isolation work of Snelson.²⁸ Snelson determined ν_2 and ν_3 to be 345 and 1555 cm⁻¹ for BeF₂, empirically correcting for matrix shifts. Remarkably, Snelson's value for ν_3 agrees exactly with the gas-phase value determined in our work. The ν_2 value of Snelson is also undoubtedly correct and, indeed, we find no evidence for ν_2 above 500 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.³⁷⁻⁴² Mass spectrometric studies³⁸⁻⁴¹ are generally consistent with dimer concentrations of 1%-2% and matrix isolation work on the dimers is available.^{19,42}

The alkaline earth dihalides have been the subject of numerous theoretical papers,^{4-7,42-62} partly because they violate simple bonding rules.⁴⁻⁷ For example, both the valence shell electron pair repulsion (VSEPR) "theory" and Walsh's rules predict linear geometries for the alkaline earth dihalides.⁴⁻⁷

Two general physical models are used to rationalize bent structures. The participation of *d* orbitals on the alkaline earth atoms^{4-7,43-45} favors nonlinear geometries as does strong polarization of the alkaline earth ion by anions.⁴⁶⁻⁵⁷ Although these simple models are physically appealing, they both have been heavily criticized. The Rittner-type⁶³ ionic models are particularly vulnerable because they use "arbitrary" values of the polarizabilities.⁵⁻⁷

II. EXPERIMENTAL

The high resolution infrared emission spectrum of BeF₂ was observed with the National Solar Observatory Fourier transform spectrometer at Kitt Peak. The unapodized 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 BeF₂ was produced in an alumina tube furnace by heating solid BeF₂ to a maximum temperature of

about 1000 °C. The apparatus used was described previously in our observation of emission spectrum of SiS.⁶⁴ 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 glower 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 glower 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 resolu-

tion-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 H₂O⁶⁵ 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, ν_3 , 001-000, $\Sigma_u^+ - \Sigma_g^+$, 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 ν_3 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 ($I = \frac{1}{2}$) 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.^{66,67} 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:

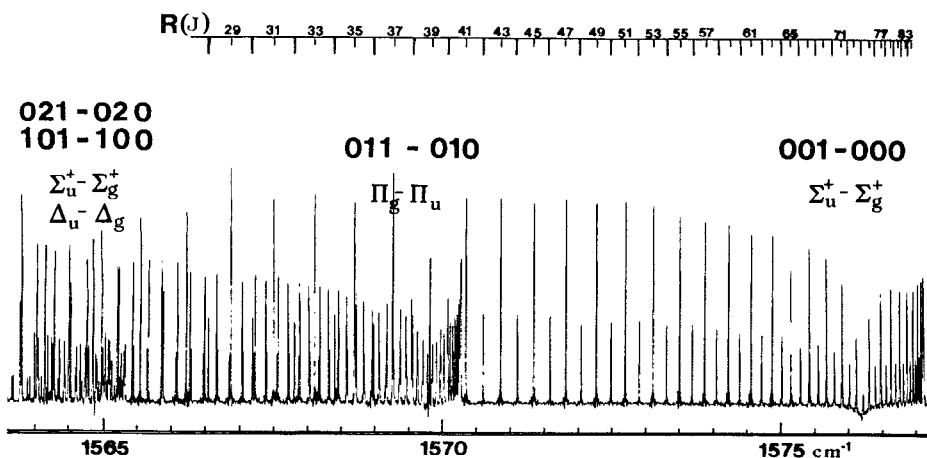
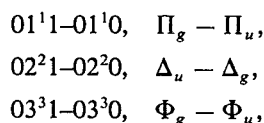


FIG. 1. Infrared emission spectrum of BeF₂ in the region of the antisymmetric stretching mode ν_3 . All of the vibrational bands make *R* heads at high *J* values. The intensity alternation due to fluorine nuclear spin statistics can be clearly seen in the fundamental band.

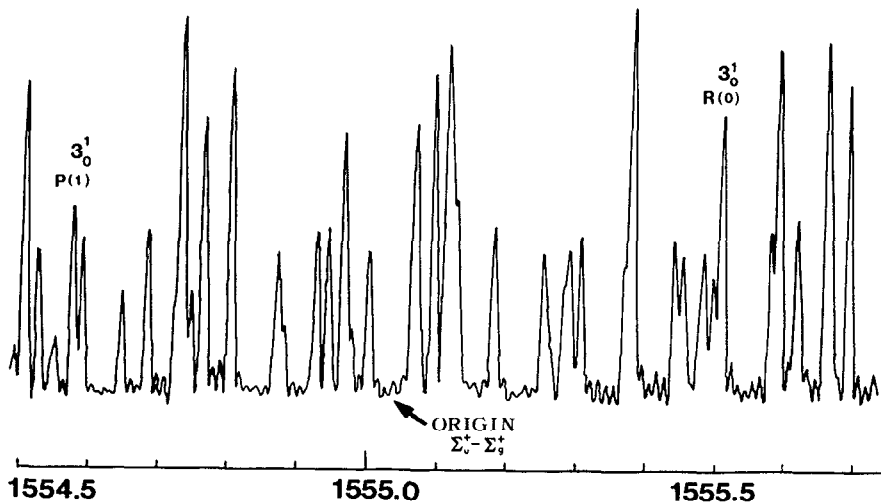
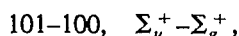
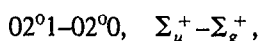
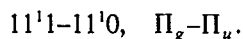
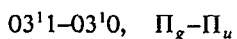


FIG. 2. An expanded portion of the infrared emission spectrum of BeF₂ near the origin of the fundamental band. The spectrum is very dense because of the overlap of many hot bands.

the Σ-Σ Fermi dyad,



and the Π-Π Fermi dyad,



The 01¹1-01¹0, Π_g-Π_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 Π_g-Π_u transitions of the Π-Π

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 CO₂.

The 02²1-02²0, Δ_u-Δ_g band shows *l*-type resonance splitting only at very high *J* values. The absolute rotational assignment for this band was made by using the α₂ value (Table II) obtained from the 001-000 and the 01¹1-01¹0 bands. The correct rotational assignment of the Δ_u-Δ_g band also showed a minimum in the variance of the fit. The 03³1-03³0, Φ_g-Φ_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 Σ_u⁺-Σ_g⁺

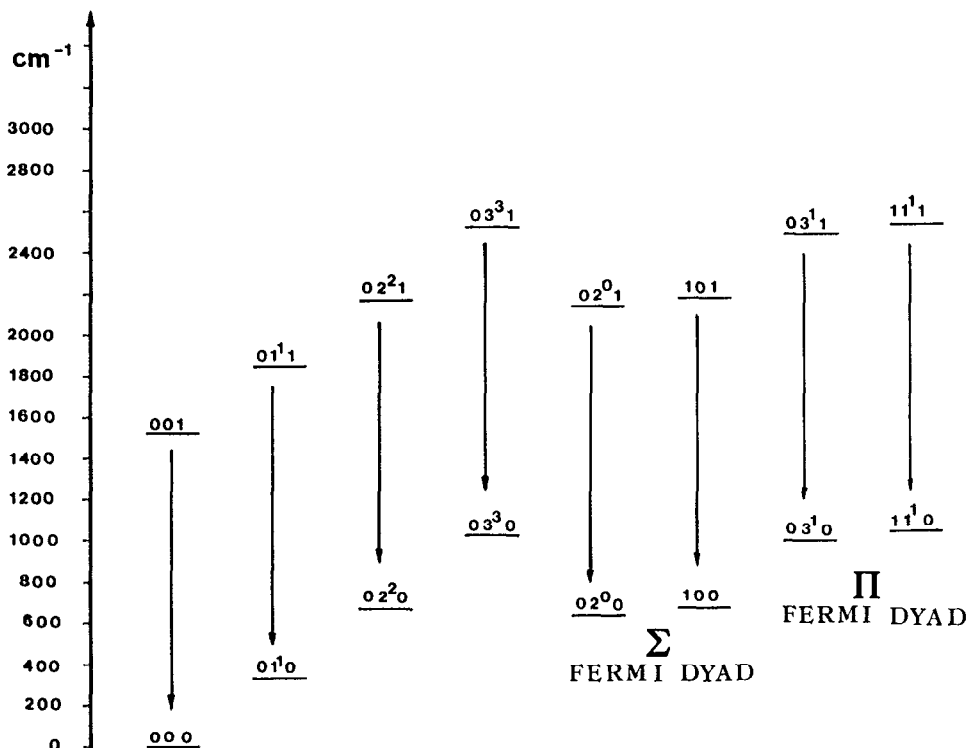


FIG. 3. An energy level diagram for BeF₂ showing the observed emission bands.

bands (02⁰1–02⁰0, 101–100) in the Σ–Σ Fermi dyad. The strong Fermi interaction perturbs the B values so that, for example, $B_{02^0 0} \neq B_{02^0 0}$. The comparison with CO₂ again proved to be indispensable in guiding our assignments.^{66,67} The $B_{02^0 0}$ value was shifted down by 0.000 943 cm⁻¹ by the mixing of the 02⁰0 and 100 vibrational wave functions. The molecular constants for the observed BeF₂ bands are provided in Table I. The line positions are available through PAPS⁶⁸ 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:

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

where $q = q_D = 0$ for Σ states; $q = 0$ for Δ states and the upper (lower) sign refers to $e(f)$ parity.⁶⁹ The l -type doubling parameter q is negative in 010 vibrational state because the f parity level lies above the e 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 CO₂, however, by Bailly and co-workers^{66,67} 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 (11¹0–000) of Π_u–Σ_g⁺ symmetry. If this

assignment is correct, then the value for ν_1 lies between 780 and 890 cm⁻¹. This value is somewhat higher than the value of 680 cm⁻¹ estimated²⁸ from the ν_3 band using the valence force approximation. A gas-phase Raman measurement of ν_1 for BeF₂ is desirable.

IV. DISCUSSION

The geometry of BeF₂ 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_{000} value. Since bands involving all three normal modes were found, it is possible to determine⁷⁰ B_e as well as α_1 , α_2 , and α_3 :

$$B_{\nu_1\nu_2\nu_3} = B_e - \alpha_1(\nu_1 + \frac{1}{2}) - \alpha_2(\nu_2 + 1) - \alpha_3(\nu_3 + \frac{1}{2}).$$

The α_2 and α_3 values (Table II) were found by using the B_{010} , B_{001} , and B_{000} values of Table I. The observed α_1 value of –0.000 148 6(103) cm⁻¹ was corrected for the effects of Fermi resonance by using the observed $B_{02^0 0} - B_{02^0 0}$ shift to provide an α_1 (corrected) = 0.000 794 3(62) cm⁻¹. The B_e of Table II results in an 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 BeF₂¹¹ provide 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,³ as well as the previous *ab initio* calculations.^{45,59–63} For the diatomic BeF molecule r_e is 1.3610 Å,⁷¹ very close to the 1.3730 Å value found in BeF₂. The unpaired electron in the X²Σ⁺ ground state of BeF is clearly nonbonding.

TABLE I. Molecular constants for BeF₂.

Level	Band* origin	$B\nu_1\nu_2\nu_3$	$10^6 D\nu_1\nu_2\nu_3$	$10^3 q_2$	$10^9 q_D$
00 ⁰ 0	1555.047 92(5)	0.234 990 66(56)	0.101 680(47)		
00 ⁰ 1		0.232 544 62(57)	0.100 878(49)		
01 ¹ 0	1547.829 96(7)	0.236 244 69(66)	0.106 464(76)	–0.384 7(13)	0.70(15)
01 ¹ 1		0.233 816 87(66)	0.105 732(78)	–0.377 6(13)	0.79(15)
02 ² 0	1540.635 86(7)	0.237 492 62(90)	0.111 050(84)		–0.402(89)
02 ² 1		0.235 084 07(91)	0.110 354(87)		–0.226 (91)
03 ³ 0	1533.465 82(7)	0.238 732 02(70)	0.115 750(62)		
03 ³ 1		0.236 342 15(71)	0.115 059(65)		
Σ–Σ FERMI DYAD					
10 ⁰ 0	1543.272 14(8)	0.235 139 26(87)	0.083 689(80)		
10 ⁰ 1		0.232 658 82(88)	0.083 049(84)		
02 ⁰ 0	1542.340 80(92)	0.236 549 71(97)	0.127 895(80)		
02 ⁰ 1		0.234 182 86(99)	0.127 254(83)		
Π–Π FERMI DYAD					
11 ¹ 0	1535.782 31(7)	0.236 428 72(91)	0.092 50(11)	–0.551 4(10)	
11 ¹ 1		0.233 978 23(93)	0.091 51(12)	–0.531 5(10)	
03 ¹ 0	1535.503 97(6)	0.237 693 22(84)	0.125 122(80)	–0.582 47(64)	
03 ¹ 1		0.235 331 14(85)	0.124 554(83)	–0.575 96(64)	

*One standard deviation error is enclosed in parentheses.

TABLE II. Equilibrium molecular constants for BeF₂ (in cm⁻¹).

B_e	=	0.235 356 8(33)
α_1 (corrected)	=	0.000 794 3(62)
α_2	=	-0.001 254 03(87)
α_3	=	0.002 446 04(80)
r_e	=	1.372 971 0(95) Å

The Π vibrational levels show l -type doubling splittings and the Δ vibrational levels display l -resonance splittings as expected for transitions associated with doubly degenerate modes.⁷⁰ For a symmetric linear triatomic molecule, the magnitude of the splitting is given by the equation⁷⁰:

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

For vibrational states of Δ symmetry, " q " = 0 and the leading term is " q_D ". For a linear, symmetric triatomic molecule such as BeF₂, the value of q is given by^{70,72}

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

Using $q_{010} = -0.3874(13)$ cm⁻¹, $B_{000} = 0.234 99$ cm⁻¹ and $\nu_3 = 1555$ cm⁻¹, Eq. (2) predicts $\nu_2 = 347$ cm⁻¹ in remarkable agreement with Snelson's value²⁸ of 345 cm⁻¹.

The detailed theory of l -resonance in Δ states was first derived by Amat and Nielsen⁷³ with later contributions by Maki and Lide.⁷⁴ The sign of q_D indicates that the 02²⁰ vibrational level lies higher in energy than the 02⁰⁰ level. In addition the changes in the centrifugal distortion constants relative to the ground state are consistent with the 100 vibrational level lying above the 020 level.

V. CONCLUSION

The high resolution infrared emission spectrum of BeF₂ vapor at 700 °C was observed with a Fourier transform spectrometer. The antisymmetric stretching mode ν_3 near 1555 cm⁻¹ and seven hot bands were rotationally analyzed. From the equilibrium rotational constant, the equilibrium Be-F bond distance of 1.372 917 0(95) Å was calculated for BeF₂. 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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- ¹M. Hargittai, *Coord. Chem. Rev.* **91**, 35 (1988).
- ²I. R. Beattie, P. J. Jones, and N. A. Young, *Angew. Chem. (Intern. Ed.)* **28**, 313 (1989).
- ³J. M. Dyke and T. G. Wright, *Chem. Phys. Lett.* **169**, 138 (1990).
- ⁴L. von Szentpaly and P. Schwerdtfeger, *Chem. Phys. Lett.* **170**, 555 (1990).
- ⁵U. Salzner and P. von R. Schleyer, *Chem. Phys. Lett.* **172**, 461 (1990).
- ⁶R. L. De Kock, M. A. Peterson, L. K. Timmer, E. J. Baerends, and P. Vernooijs, *Polyhedron* **9**, 1919 (1990).
- ⁷D. M. Hassett and C. J. Marsden, *Chem. Comm.* **1990**, 667.
- ⁸C. W. Bauschlicher, Jr., and B. O. Roos, *J. Chem. Phys.* **91**, 4785 (1989).
- ⁹C. W. Bauschlicher, Jr., M. Rosi, and S. R. Langhoff, *Chem. Phys.* **146**, 237 (1990).
- ¹⁰F. J. Grieman, S. H. Ashworth, J. M. Brown, and I. R. Beattie, *J. Chem. Phys.* **92**, 6365 (1990); F. Grieman and J. Brown (private communication).
- ¹¹P. A. Akishin, V. P. Spiridonov, and G. A. Sobolev, *Dokl. Akad. Nauk. SSSR* **118**, 1134 (1958); P. A. Akishin and V. P. Spiridonov, *Kristallografiya* **2**, 475 (1957).
- ¹²L. Wharton, R. A. Berg, and W. Klemperer, *J. Chem. Phys.* **39**, 2023 (1963).
- ¹³A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Am. Chem. Soc.* **86**, 4544 (1964).
- ¹⁴A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Chem. Phys.* **40**, 3471 (1964).
- ¹⁵P. J. Dagdigian and L. Wharton, *J. Chem. Phys.* **58**, 1243 (1973).
- ¹⁶F. Ramondo, L. Bencivenni, S. Nunziante Cesaro, and K. Hilbert, *J. Mol. Struct.* **192**, 83 (1989).
- ¹⁷D. L. Cocke, C. A. Chang, and K. A. Gingerich, *Appl. Spectrosc.* **27**, 260 (1973).
- ¹⁸V. I. Baikov, *Opt. Spectrosc.* **25**, 194 (1968); **27**, 502 (1969).
- ¹⁹F. Ramondo, V. Rossi, and L. Bencivenni, *Mol. Phys.* **64**, 513 (1988).
- ²⁰D. E. Mann, G. V. Calder, K. S. Seshadri, D. White, and J. J. Linevsky, *J. Chem. Phys.* **46**, 1138 (1967).
- ²¹V. Calder, D. E. Mann, K. S. Seshadri, M. Allavena, and D. White, *J. Chem. Phys.* **51**, 2093 (1969).
- ²²D. White, G. V. Calder, S. Hemple, and D. E. Mann, *J. Chem. Phys.* **59**, 6645 (1973).
- ²³S. P. Randall, F. T. Green, and J. L. Margrave, *J. Phys. Chem.* **63**, 758 (1959).
- ²⁴R. H. Hauge, J. L. Margrave, and A. S. Kana'an, *J. Chem. Soc. Faraday* **2**, **71**, 1082 (1975).
- ²⁵J. W. Hastie, R. H. Hauge, and J. L. Margrave, *High Temp. Sci.* **3**, 56, 257 (1971).
- ²⁶M. Astier, G. Berthier, and P. Millie, *J. Chem. Phys.* **57**, 5008 (1972).
- ²⁷A. Büchler and W. Klemperer, *J. Chem. Phys.* **29**, 121 (1958).
- ²⁸A. Snelson, *J. Phys. Chem.* **70**, 3208 (1966); **72**, 251 (1968).
- ²⁹I. Eliezer and A. Reger, *Coord. Chem. Rev.* **9**, 189 (1972).
- ³⁰M. L. Lesiecki and J. W. Nibler, *J. Chem. Phys.* **64**, 871 (1976).
- ³¹V. P. Spiridonov, A. G. Gershikov, A. B. Altman, G. V. Romanov, and A. A. Ivanov, *Chem. Phys. Lett.* **77**, 41 (1981).
- ³²V. V. Kasparov, Y. S. Ezhov, and N. G. Rambidi, *J. Struct. Chem.* **20**, 217, 288 (1979); **21**, 154 (1980).
- ³³V. I. Bazhanov, *J. Struct. Chem.* **27**, 208 (1986).
- ³⁴E. Vajda, M. Hargittai, I. Hargittai, J. Tremmel, and J. Brunvoll, *Inorg. Chem.* **26**, 1171 (1987).
- ³⁵C. A. Hammer, J. D. Allen, Jr., L. C. Cusachs, and G. K. Schweitzer, *J. Electron Spectrosc. Relat. Phenom.* **13**, 149 (1978).
- ³⁶E. P. F. Lee and A. W. Potts, *Proc. R. Soc. London Ser. A* **365**, 395 (1979).
- ³⁷L. Brewer, G. R. Somayajulu, and E. Brackett, *Chem. Rev.* **63**, 111 (1963).
- ³⁸H. H. Emons, D. Kiessling, and W. Horlbeck, *Z. Anorg. Allg. Chem.* **488**, 219 (1982).
- ³⁹D. L. Hildenbrand and L. P. Theard, *J. Chem. Phys.* **42**, 3230 (1965).
- ⁴⁰J. Berkowitz and J. R. Marquart, *J. Chem. Phys.* **37**, 1853 (1962).
- ⁴¹G. D. Blue, J. W. Green, R. G. Bautista, and J. L. Margrave, *J. Phys. Chem.* **67**, 877 (1963).
- ⁴²A. Snelson, B. N. Cyvin, and S. J. Cyvin, *Z. Anorg. Allg. Chem.* **410**, 206 (1974).
- ⁴³C. A. Coulson, *Isr. J. Chem.* **11**, 683 (1973).
- ⁴⁴E. F. Hayes, *J. Phys. Chem.* **70**, 3740 (1966).
- ⁴⁵J. L. Gole, A. K. Q. Siu, and E. F. Hayes, *J. Chem. Phys.* **58**, 857 (1973).
- ⁴⁶T. E. Brackett and E. B. Brackett, *J. Phys. Chem.* **66**, 1542 (1962).

- ⁴⁷D. Cubicciotti, *J. Phys. Chem.* **65**, 1058 (1961).
- ⁴⁸A. Büchler, W. Klemperer, and A. G. Emslie, *J. Chem. Phys.* **36**, 2499 (1962).
- ⁴⁹M. Guido and G. Gigli, *J. Chem. Phys.* **65**, 1397 (1976).
- ⁵⁰Y. S. Kim and R. G. Gordon, *J. Chem. Phys.* **60**, 4332 (1974).
- ⁵¹I. Eliezer, *Theor. Chim. Acta* **18**, 77 (1970).
- ⁵²I. Eliezer and A. Reger, *Theor. Chim. Acta* **26**, 283 (1972).
- ⁵³G. Galli and M. P. Tosi, *Il Nuovo Cimento* **4D**, 413 (1984).
- ⁵⁴W. Andreoni, G. Galli, and M. Tosi, *Phys. Rev. Lett.* **55**, 1734 (1985).
- ⁵⁵M. Spoliti, G. DeMaria, L. D'Alessio, and M. Maltese, *J. Mol. Struct.* **67**, 159 (1980).
- ⁵⁶D. L. Hildenbrand, *J. Electrochem. Soc.* **126**, 1396 (1979).
- ⁵⁷M. C. Drake and G. M. Rosenblatt, in *Proc. Symp. on High Temperature Metal Halide Chemistry*, edited by D. L. Hildenbrand and D. Cubicciotti, Proc. Vol. **78/1**, (Electrochemical Society, Princeton, NJ 1978).
- ⁵⁸V. G. Solomonik, V. M. Ozerova, and K. S. Krasnov, *Russ. J. Phys. Chem.* **56**, 879 (1982).
- ⁵⁹V. G. Solomonik, *J. Struct. Chem.* **24**, 25 (1983).
- ⁶⁰S. Canuto and M. Braga, *J. Mol. Struct.* **88**, 209 (1982).
- ⁶¹S. D. Peyerimhoff, R. J. Buenker, and J. L. Whitten, *J. Chem. Phys.* **46**, 1707 (1967).
- ⁶²K. Hashimoto, Y. Osamura, and S. Iwata, *J. Mol. Struct.* **152**, 101 (1987).
- ⁶³E. S. Rittner, *J. Chem. Phys.* **19**, 1030 (1951).
- ⁶⁴C. I. Frum, R. Engleman, Jr., and P. F. Bernath, *J. Chem. Phys.* **93**, 5457 (1990).
- ⁶⁵G. Guelachvili and K. N. Rao, *Handbook of Infrared Standards* (Academic, Orlando, FL, 1986).
- ⁶⁶D. Bailly, R. Farrenq, G. Guelachvili, and C. Rossetti, *J. Mol. Spectrosc.* **90**, 74 (1981).
- ⁶⁷D. Bailly and C. Rossvetti, *J. Mol. Spectrosc.* **102**, 392 (1983).
- ⁶⁸See AIP document no. PAPS JCPSA-95-1435-46 for 46 pages of Order by PAPS number and journal reference from American Institute of Physics, Physics Auxiliary Publication Service, 335 East 45th Street, New York, NY 10017. The price is \$1.50 for each microfiche (98 pages) or \$5.00 for photocopies of up to 30 pages, and \$0.15 for each additional page over 30 pages. Airmail additional. Make checks payable to the American Institute of Physics.
- ⁶⁹J. M. Brown, J. T. Hougen, K. P. Huber, J. W. C. Johns, I. Kopp, H. Lefebvre-Brion, A. J. Merer, D. A. Ramsay, J. Rostas, and R. N. Zare, *J. Mol. Spectrosc.* **55**, 500 (1975).
- ⁷⁰G. Herzberg, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, (Van Nostrand Reinhold, New York, 1966).
- ⁷¹K. P. Huber and G. Herzberg, *Constants of Diatomic Molecules* (Van Nostrand Reinhold, New York, 1979).
- ⁷²D. Papousek and M. R. Aliev, *Molecular Vibrational-Rotational Spectra* (Elsevier, Amsterdam, 1982).
- ⁷³G. Amat and H. H. Nielsen, *J. Mol. Spectrosc.* **2**, 163 (1958).
- ⁷⁴A. G. Maki, Jr., and D. R. Lide, Jr., *J. Chem. Phys.* **47**, 3206 (1967).