# The Structure of Krypton Difluoride[1a]

**Craig Murchison,[1b] Sandor Reichman,[1b] Dennis Anderson,[1b] John Overend,[1b] and Felix Schreiner[1c]**

*Contribution from the Molecular Spectroscopy Laboratory, School of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455, and Argonne National Laboratory, Argonne, Illinois 60439.* *Received May 8, 1968*

**Abstract:** The band at *ca.* 590 cm$^{-1}$ in the infrared spectrum of $^{86}KrF_2$ has been studied with a resolution of 0.08 cm$^{-1}$. From the rotational fine structure it is clear that $KrF_2$ is a linear molecule and the two fluorine atoms are symmetrically equivalent. The analysis of the band gives $\nu_0 = 589.889$, $B_0 = 0.12626$, $B' = 0.12575$, and $D_0 = D' = 7.8 \times 10^{-8}$ cm$^{-1}$ as the most probable set of constants, although we cannot rule out a second set of constants corresponding to an alternative assignment. From these results we conclude that the length of the KrF bond, $r_0$, is equal to 1.875 ± 0.002 Å, or possibly 1.867 ± 0.002 Å.

This high-resolution study of the $\nu_3$ fundamental band in the infrared spectrum of $KrF_2$ was undertaken with the express purpose of determining a precise estimate of the KrF bond length. Previously Claassen, Goodman, Malm, and Schreiner[2] had obtained a low-resolution, gas-phase infrared spectrum of the compound and found the separation of the PR maxima in the unresolved contour of the $\nu_3$ band to be 15.5 ± 0.5 cm$^{-1}$, corresponding to a KrF bond length of about 1.9 Å. They also obtained Raman spectra of $KrF_2$[2] and were able to assign very satisfactorily all the features in the infrared and Raman spectra on the basis of a linear symmetric ($D_{\infty h}$) structure. From this evidence it seems certain that this is the geometrical structure of the $KrF_2$ molecule in the gas phase; what remains is to fix more precisely the single geometrical parameter—the length of the KrF bond—and to do this we need just one rotational constant.

## Experimental Section

We picked the $\nu_3$ band (hereafter $\nu_3$ will denote the transition 001 ← 000) as the one most likely to yield the desired information. It lies at about 590 cm$^{-1}$ in a region where the effective resolving power of our instrument is about 0.05 cm$^{-1}$, it is relatively intense, and it does not appear to be overlapped by other bands. From the approximate geometry[2] we calculate the basic spacing of the rotational fine structure, $2B$, to be *ca.* 0.25 cm$^{-1}$ and to be fairly easily resolved. There are, however, two expected sources of complication of the high-resolution spectrum. Natural krypton contains a number of isotopes in similar abundance ($^{78}$Kr 0.4%, $^{80}$Kr 2.3%, $^{82}$Kr 11.6%, $^{83}$Kr 11.6%, $^{84}$Kr 56.9%, $^{86}$Kr 17.4%) and, since the $\nu_3$ antisymmetric KrF stretching mode involves considerable motion of the krypton atom, the harmonic frequencies of the isotopic molecules will differ slightly. The second expected complication is the appearance of hot bands, since several excited vibrational states are expected to be significantly populated at room temperature. From the observed vibrational frequencies (cm$^{-1}$), $\nu_1$ 449, $\nu_2$ 232.6, and $\nu_3$ 588, we estimate, in the double-harmonic approximation, the intensities of the most important hot bands relative to the $\nu_3$ transition to be as follows: $\nu_3 + \nu_2 \leftarrow \nu_2$; $(\pi \leftarrow \pi)$ 62%, $\nu_3 + 2\nu_2 \leftarrow 2\nu_2$; $(\Sigma \leftarrow \Sigma)$ 10%; $(\Delta \leftarrow \Delta)$ 20%, $\nu_3 + \nu_1 \leftarrow \nu_1$; $(\Sigma \leftarrow \Sigma)$ 10%. Anharmonicity will shift these hot bands slightly from the main $\nu_3$ band, further complicating the spectrum.

Consideration of these probable complications led us to procure, at the outset, a sample of isotopically pure $^{86}$Kr from which about 2 mmoles of $^{86}KrF_2$ was prepared by a method described in the literature.[3] In addition, we prepared a relatively large quantity of $KrF_2$ as a natural isotopic mixture. The samples were prepared at Argonne National Laboratory and stored at Dry Ice temperature in Kel-F [poly(trifluorochloroethylene)] U tubes of 4-mm i.d. and 1-mm wall thickness. The Kel-F U tubes were part of a small nickel manifold to which was attached a 40-mm path length nickel absorption cell with AgCl windows. The absorption cell and manifold were set up and tested at Argonne National Laboratory and then transported along with the samples to the University of Minnesota where the cell was set in place in the 2.5-m high-resolution infrared spectrometer.[4]

We had designed the special nickel cell with the associated manifold to fit into the small space between the exit window of the spectrometer vacuum tank and the optics used to transfer the radiation to the liquid-helium-cooled copper-doped germanium detector. In this way we were able to obtain free access to the sample and the vacuum line at all times during the experiment.

We had no means of measuring the sample pressure, and our procedure was to set the spectrometer on a frequency in the $\nu_3$ band at which there was absorption and then to follow the admission of the sample into the cell by the decrease in transmission. We were also able to follow, in the same way, the decomposition of the sample to transparent Kr and $F_2$. The first samples introduced into the cell had a half-life of only a few seconds, but, as the cell became seasoned, we found the sample half-life became of the order of 30-40 min.[3] Under these conditions we felt that useful spectra could be obtained, although the difficulties with handling the sample did cause us to lose some resolution.[5] The spectrum of the $\nu_3$ band shown in Figure 1 is a composite of several sections, each obtained with a different sample. Within each section there is a decay of sample from high frequency to low frequency, and there are of course differences in sample pressure from one section to the next. Nevertheless, we have tried, in picking out this composite spectrum from the ones we measured, to match the relative intensities throughout the band, and probably the varying sample concentration can be disregarded to first order; but this limitation should be kept in mind when interpreting the details of the spectrum.

The spectrum of $KrF_2$ was measured in the third order of the 30-line/mm grating and calibrated against the $\nu_2$ band of HCN measured in fourth order.[6]

## Results

If krypton difluoride is, indeed, a linear symmetrical molecule, we expect the band due to the transition $\nu_3$ to

---

[1] (a) The spectroscopic part of this work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Grant No. 570-67; the preparative part and some subsequent experimental phases were supported by the U. S. Atomic Energy Commission; (b) University of Minnesota; (c) Argonne National Laboratory.

[2] H. H. Claassen, G. L. Goodman, J. G. Malm, and F. Schreiner, *J. Chem. Phys.*, **42**, 1229 (1965).

[3] F. Schreiner, J. G. Malm, and J. C. Hindman, *J. Am. Chem. Soc.*, 87, 25 (1965).

[4] J. Overend, *et al.*, *Appl. Opt.*, **6**, 457 (1967).

[5] The special absorption cell used for this problem reduced considerably the intensity of the radiation falling on the detector. In addition, we were unable to use a long time constant on account of the instability of the sample. We estimate the effective resolution of the instrument at 0.08 cm$^{-1}$, about twice the normal resolution in this spectral region.

[6] W. W. Brimm, J. M. Hoffman, H. H. Nielsen, and K. N. Rao, *J. Opt. Soc. Am.*, **50**, 1208 (1960).

exhibit an alternation in intensity, the lines originating in odd $J$ states having three times the statistical weight of those originating in even $J$ states. We should not see any intensity alternation in the hot bands since we should not resolve the $l$-type doublets.[7] Accordingly, the lines of the principal hot band $\nu_2 + \nu_3 \leftarrow \nu_2$ should appear slightly more intense (1.3:1) than the even $J$ lines of the main band and about half as intense (4:9) as the odd $J$ lines. This model appears to account quite satisfactorily for the general appearance of the spectrum in Figure 1; the over-all beat pattern suggests alternating reinforcement and interference of just two similarly intense bands which we take as $\nu_3$ and $\nu_3 + \nu_2 \leftarrow \nu_2$. The other hot bands do not appear to make an important contribution to the over-all pattern but will certainly show in details. If we examine the regions of reinforcement in the spectrum, we find that some show the twofold statistical intensity alternation expected in the $\nu_3$ transition (*i.e.*, between 596.32 and 600.56 and 583.83 and 587.57 cm$^{-1}$) whereas other regions show little, if any, evidence of twofold intensity alternation (*i.e.*, between 591.89 and 594.74 cm$^{-1}$). Also, in the extreme wing of the P branch, the $\nu_3 + \nu_2 \leftarrow \nu_2$ lines are considerably stronger than those of $\nu_3$ and in the R branch wing the opposite situation obtains.

From these observations we conclude that the center of the $\nu_3 + \nu_2 \leftarrow \nu_2$ band lies significantly (about ten rotational lines) to the low-frequency side of the center of the $\nu_3$ band. From the low-resolution spectra[2] we expect the center of the $\nu_3$ band to be close to 590 cm$^{-1}$, and in that region of our spectrum the prominent lines do not exhibit intensity alternation and can therefore reasonably be assigned to the $\nu_3 + \nu_2 \leftarrow \nu_2$ band. In that case, the origin of the $\nu_3 + \nu_2 \leftarrow \nu_2$ band should be in the region 585.5–587.3 cm$^{-1}$, and here the prominent lines alternate in intensity and can be assigned to $\nu_3$.

With these general ideas established, we proceeded to pick out a series of lines of $\nu_3$ in the P branch and a similar one in the R branch. These assignments are shown in Figure 1 as full lines. We were able to follow each series up to within a few lines of the band center, and we are confident of our interpolation between the two branches. The next step was to find the band origin and establish the absolute assignment of the rotational lines. There are three criteria for the selection of the band origin: (i) there should be a central gap between $R_0$ and $P_1$, (ii) the intensity alternation pattern has to change over since there is the central gap and the weak $R_0$ line between the strong $P_1$ and $R_1$ lines, and (iii) the band origin must be in a region in which the lines of $\nu_3$ are weak with respect to those of $\nu_3 + \nu_2 \leftarrow \nu_2$. From criteria ii and iii we conclude that the band origin must be between 588.9 and 591.9 cm$^{-1}$. Requirement i narrows this range to just two possibilities. The band center is either in the gap at 589.4 cm$^{-1}$ or it is on the red side of the line at 589.9 cm$^{-1}$. We prefer the second assignment because with this assignment we can explain the observation that the lines at 589.7 and 590.4 cm$^{-1}$ are broad, but the two lines in between at 590.2 and 589.9 cm$^{-1}$ are relatively sharp, if we assign the broad lines to blends of the hot-band lines with the intense main-band lines $P_1$ and $R_1$. Nevertheless, we cannot completely exclude the alternative assignment, and we have used both in the analysis of our data. The results are shown in Tables I and II.

**Table I.** Observed Frequencies (cm$^{-1}$) of the Band $\nu_3$ and Their Assignment

| | P($J$) | | | R($J$) | |
|---|---|---|---|---|---|
| Frequency | Assignment I | Assignment II | Frequency | Assignment I | Assignment II |
| | | | 589.62 | | 0 |
| 574.54 | 55 | 53 | 590.38 | 1 | 3 |
| 574.86 | 54 | 52 | 590.63 | 2 | 4 |
| 575.15 | 53 | 51 | 590.89 | 3 | 5 |
| 575.46 | 52 | 50 | 591.16 | 4 | 6 |
| 575.75 | 51 | 49 | 591.40 | 5 | 7 |
| 576.06 | 50 | 48 | 591.64 | 6 | 8 |
| 576.36 | 49 | 47 | 591.84 | 7 | 9 |
| 576.65 | 48 | 46 | 592.10 | 8 | 10 |
| 576.95 | 47 | 45 | 592.35 | 9 | 11 |
| 577.24 | 46 | 44 | 592.58 | 10 | 12 |
| 577.54 | 45 | 43 | 592.84 | 11 | 13 |
| 577.84 | 44 | 42 | 593.08 | 12 | 14 |
| 578.15 | 43 | 41 | 593.32 | 13 | 15 |
| 578.44 | 42 | 40 | 593.53 | 14 | 16 |
| 578.73 | 41 | 39 | 593.79 | 15 | 17 |
| 579.02 | 40 | 38 | 594.03 | 16 | 18 |
| 579.31 | 39 | 37 | 594.26 | 17 | 19 |
| 579.60 | 38 | 36 | 594.53 | 18 | 20 |
| 579.88 | 37 | 35 | 594.74 | 19 | 21 |
| 580.16 | 36 | 34 | 594.98 | 20 | 22 |
| 580.45 | 35 | 33 | 595.17 | 21 | 23 |
| 580.73 | 34 | 32 | 595.41 | 22 | 24 |
| 581.02 | 33 | 31 | 595.62 | 23 | 25 |
| 581.31 | 32 | 30 | 595.88 | 24 | 26 |
| 581.59 | 31 | 29 | 596.10 | 25 | 27 |
| 581.90 | 30 | 28 | 596.32 | 26 | 28 |
| 582.17 | 29 | 27 | 596.53 | 27 | 29 |
| 582.44 | 28 | 26 | 596.74 | 28 | 30 |
| 582.72 | 27 | 25 | 596.97 | 29 | 31 |
| 583.02 | 26 | 24 | 597.19 | 30 | 32 |
| 583.28 | 25 | 23 | 597.43 | 31 | 33 |
| 583.56 | 24 | 22 | 597.62 | 32 | 34 |
| 583.83 | 23 | 21 | 597.86 | 33 | 35 |
| 584.11 | 22 | 20 | 598.06 | 34 | 36 |
| 584.39 | 21 | 19 | 598.29 | 35 | 37 |
| 584.66 | 20 | 18 | 598.51 | 36 | 38 |
| 584.92 | 19 | 17 | 598.71 | 37 | 39 |
| 585.20 | 18 | 16 | 598.95 | 38 | 40 |
| 585.47 | 17 | 15 | 599.15 | 39 | 41 |
| 585.72 | 16 | 14 | 599.37 | 40 | 42 |
| 585.99 | 15 | 13 | 599.56 | 41 | 43 |
| 586.23 | 14 | 12 | 599.75 | 42 | 44 |
| 586.52 | 13 | 11 | 599.95 | 43 | 45 |
| 586.77 | 12 | 10 | 600.15 | 44 | 46 |
| 587.06 | 11 | 9 | 600.37 | 45 | 47 |
| 587.30 | 10 | 8 | 600.56 | 46 | 48 |
| 587.57 | 9 | 7 | 600.80 | 47 | 49 |
| 587.82 | 8 | 6 | 600.98 | 48 | 50 |
| 588.12 | 7 | 5 | 601.19 | 49 | 51 |
| 588.39 | 6 | 4 | 601.59 | 51 | 53 |
| 588.62 | 5 | 3 | 601.79 | 52 | 54 |
| 588.87 | 4 | 2 | 601.98 | 53 | 55 |
| 589.12 | 3 | 1 | 602.17 | 54 | 56 |
| 589.62 | 1 | | 602.37 | 55 | 57 |
| | | | 602.54 | 56 | 58 |
| | | | 602.72 | 57 | 59 |
| | | | 602.91 | 58 | 60 |
| | | | 603.09 | 59 | 61 |
| | | | 603.30 | 60 | 62 |
| | | | 603.49 | 61 | 63 |

The assignment of the hot band is more difficult, in that there is no clear evidence from the spectrum by which the origin can be unambiguously located. In

---

[7] Using Herzberg's formula, (G. Herzberg, "Electronic Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1966, p 70), the $l$-type doubling constant $q$ is calculated to be only $2.4 \times 10^{-4}$ cm$^{-1}$.

Table II. Band Constants (cm$^{-1}$) of the Main Band $\nu_3$ of $KrF_2$

| | Assignment I | | Assignment II | |
|---|---|---|---|---|
| | Constant | Dispersion[a] | Constant | Dispersion[a] |
| $\nu_0$ | 589.889 | $4.7 \times 10^{-3}$ | 589.383 | $4.7 \times 10^{-3}$ |
| $B_{000}$ | 0.12626 | $1.5 \times 10^{-4}$ | 0.12728 | $1.4 \times 10^{-4}$ |
| $B_{001}$ | 0.12575 | $1.5 \times 10^{-4}$ | 0.12677 | $1.4 \times 10^{-4}$ |
| $\alpha_3$ | $5.08 \times 10^{-4}$ | $3.1 \times 10^{-6}$ | $5.06 \times 10^{-4}$ | $3.2 \times 10^{-6}$ |
| $D_0$ | $7.8 \times 10^{-8}$ | $3.1 \times 10^{-8}$ | $7.8 \times 10^{-8}$ | $3.1 \times 10^{-8}$ |

[a] Dispersions are estimated by assuming that the error in the individual frequencies is 0.03 cm$^{-1}$.

the wing of the P branch, the spectrum is relatively open, and between 576.9 and 584.1 cm$^{-1}$ there is a distinct series of lines which do not show intensity alternation and which can definitely be assigned to the strongest hot band $\nu_3 + \nu_2 \leftarrow \nu_2$. This series of lines blends with the main band at higher frequencies, and it is not possible to follow it without ambiguity; we cannot be certain that the numbering of the rotational lines remains sequential as the hot band passes in and out of phase with the main-band. In contrast, the sequential numbering of the main-band lines is much easier since, in addition to the greater intensity, there is the twofold intensity alternation pattern as a guide.

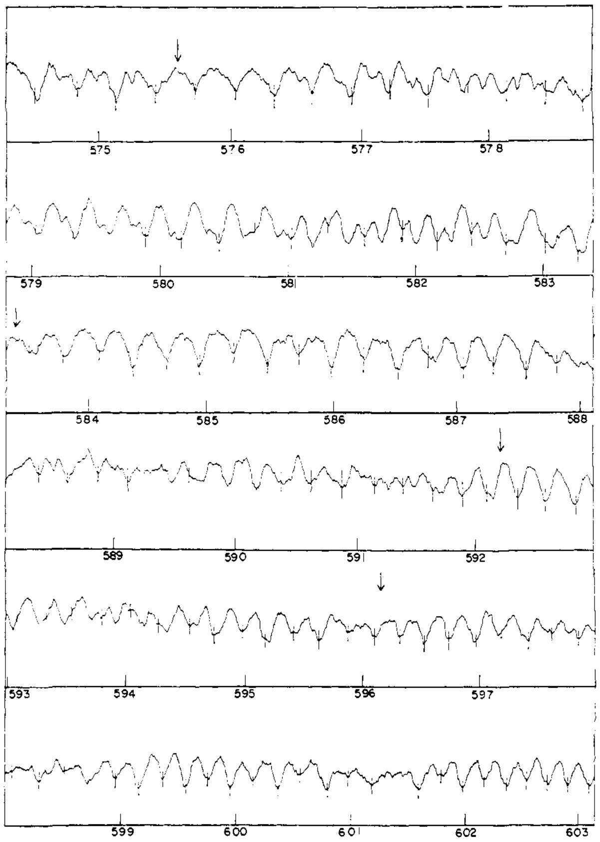

Figure 1. $\nu_3$ band of $KrF_2$, scanned from high to low frequency. Arrows indicate addition of fresh sample to absorption cell. Vertical lines through absorption bands indicate positions of $\nu_3$ rotational lines. Horizontal scale is frequency in cm$^{-1}$; vertical scale is per cent transmission; path length 40 mm; sample pressure unknown.

The $\nu_3 + \nu_2 \leftarrow \nu_2$ band results from a $\pi$–$\pi$ transition and is expected to show a weak central *Q* branch, which, from the preceding arguments, is expected to fall on the low-frequency side of the main-band origin. Our spectrum shows three features, any of which may be the Q branch of the $\nu_3 + \nu_2 \leftarrow \nu_2$ hot band, at 586.8, 588.0, and 588.5 cm$^{-1}$. These three possible assignments of the central Q branch correspond, respectively, with the assignment of the line at 584.13 cm$^{-1}$ to $P_{10}$, $P_{15}$, or $P_{17}$, and with the subsequent lines in the series numbered sequentially. Table III shows the observed line frequencies and the three possible assignments, designated, respectively, I, II, and III.

Table III. Observed P-Branch Frequencies of the Transition $\nu_3 + \nu_3 \longleftarrow \nu_2$ (cm$^{-1}$)

| Frequency | Assignment I | Assignment II | Assignment III |
|---|---|---|---|
| 584.13 | 10 | 15 | 17 |
| 583.86 | 11 | 16 | 18 |
| 583.59 | 12 | 17 | 19 |
| 583.32 | 13 | 18 | 20 |
| 583.07 | 14 | 19 | 21 |
| 582.80 | 15 | 20 | 22 |
| 582.54 | 16 | 21 | 23 |
| 582.28 | 17 | 22 | 24 |
| 582.01 | 18 | 23 | 25 |
| 581.73 | 19 | 24 | 26 |
| 581.47 | 20 | 25 | 27 |
| 581.19 | 21 | 26 | 28 |
| 580.91 | 22 | 27 | 29 |
| 580.64 | 23 | 28 | 30 |
| 580.36 | 24 | 29 | 31 |
| 580.08 | 25 | 30 | 32 |
| 579.80 | 26 | 31 | 33 |
| 579.52 | 27 | 32 | 34 |
| 579.22 | 28 | 33 | 35 |
| 578.94 | 29 | 34 | 36 |
| 578.65 | 30 | 35 | 37 |
| 578.37 | 31 | 36 | 38 |
| 578.09 | 32 | 37 | 39 |
| 577.81 | 33 | 38 | 40 |
| 577.52 | 34 | 39 | 41 |
| 577.23 | 35 | 40 | 42 |
| 576.93 | 36 | 41 | 43 |

We were able to obtain estimates of the band constants of the $\nu_3 + \nu_2 \leftarrow \nu_2$ hot band only by fitting the line frequencies to a polynomial and constraining $(B' - B'')$ and $D$ at the values obtained for the main band. Table IV shows the constants so obtained. The value of $B''$ changes by $-5\alpha_3$ or $-7\alpha_3$ as we change the assignment of the line at 584.13 cm$^{-1}$ from $P_{10}$ to $P_{15}$ or $P_{17}$, as expected.

Our preference is for the first hot-band assignment (I) since this puts the origin of the hot band about 12 lines to the low-frequency side of the main-band origin whereas the other two assignments bring the origins of the $\nu_3$ and $\nu_3 + \nu_2 \leftarrow \nu_2$ bands much closer. Thus the first assignment is the only one consistent with the general observation, made above, that the observed

**Table IV.** Band Constants (cm$^{-1}$) for the Hot Band $\nu_3 + \nu_2 \leftarrow \nu_2$[a]

| | Assignment I | Assignment II | Assignment III |
|---|---|---|---|
| $B_{01'0}$ | 0.1269 ± 0.0006 | 0.1244 ± 0.0006 | 0.1234 ± 0.0006 |
| $\nu_0$ | 586.72 ± 0.03 | 587.98 ± 0.03 | 588.47 ± 0.03 |

[a] $\alpha_3$ and $D$ constrained to $5.079 \times 10^{-4}$ and $7.82 \times 10^{-9}$ cm$^{-1}$, respectively.

beat pattern of the $\nu_3$ and $\nu_3 + \nu_2 \leftarrow \nu_2$ bands can be explained if the origins of the two bands are separated by about ten lines.

## Discussion

The main purpose of this work was to measure accurately the rotational constant $B_0$ in order to determine $r_0$, the krypton–fluorine bond length. The error in $B_0$ may be larger than that indicated by the dispersion due to systematic errors in line frequencies caused by the overlap of rotational lines. Consequently, we have taken the error in $r_0$ to be twice that indicated by the dispersion in $B_0$.

Our preferred bond length, obtained from assignment I, is 1.875 ± 0.002 Å, but it is not possible to rule out with certainty the other value 1.867 ± 0.002 Å, given by our less preferred assignment II. This bond length should be compared to the recent electron diffraction value of 1.889 ± 0.010 Å given by Bauer and coworkers.[8] The discrepancy may be due partly to experimental uncertainty, but it must be remembered that the $r_g$ obtained by electron diffraction is always larger than the spectroscopic $r_0$.[9]

Tables II and IV show that our preferred values of $B_{000}$ and $B_{01'0}$ give the smallest value of $\alpha_2$, *i.e.*, $-6 \times 10^{-4} \pm 8 \times 10^{-4}$ cm$^{-1}$. Nielsen[10] has derived an expression for $\alpha_2$ showing that anharmonicity affects the value of $\alpha_2$ only through the normal coordinate force constant $\mathbf{k}_{122}$. This constant must be small to explain the absence of strong Fermi resonance between $\nu_1$ and $2\nu_2$.[11] Letting $\mathbf{k}_{122}$ be equal to 9 cm$^{-1}$, as calculated from quadratic internal coordinate force constants only, we found $\alpha_2$ to be $-3 \times 10^{-7}$ cm$^{-1}$.

We also made an attempt to calculate $x_{23}$ which determines the separation of the main band and the ($\nu_3 + \nu_2 \leftarrow \nu_2$) hot band. For a linear XY$_2$ molecule $x_{23}$ is given by

$$x_{23} = \mathbf{k}_{2233} - \frac{2\mathbf{k}_{122}\mathbf{k}_{133}}{\omega_1} + \frac{B\omega_3}{\omega_2} + \frac{B\omega_2}{\omega_3}$$

The force constants $\mathbf{k}_{2233}$ and $\mathbf{k}_{133}$ strongly depend on the Morse parameter $a$, which we calculated from our observed value of $\alpha_3$, to be 2.54 Å$^{-1}$. This, together with our quadratic force constants,[2] gives $\mathbf{k}_{2233} = -3.29$ cm$^{-1}$, $\mathbf{k}_{133} = -91.72$ cm$^{-1}$, and $x_{23} = -1.08$ cm$^{-1}$. To obtain better agreement with our observed $x_{23} = -3.17$ cm$^{-1}$, we probably need a smaller value of $\mathbf{k}_{122}$. This may be accomplished by including the internal coordinate force constant $k_{122}$ in the potential energy expression. Assuming a value of $-0.67$ mdyn/rad$^2$ for the internal coordinate force constant $k_{122}$, which makes the normal coordinate force constant, $\mathbf{k}_{122}$, zero, $x_{23}$ is calculated to be $-2.93$ cm$^{-1}$, in good agreement with the observed $x_{23}$. This simple calculation of $x_{23}$ further indicates that the normal coordinate force constant $\mathbf{k}_{122}$ for krypton difluoride is very small, even smaller than that calculated from quadratic force constants alone.

**Acknowledgment.** We wish to thank Dr. H. H. Claassen for suggesting this work to us.

---

[8] W. Harshbarger, R. K. Bohn, and S. H. Bauer, *J. Am. Chem. Soc.*, **89**, 6466 (1967).

[9] D. R. Herschbach and V. W. Laurie, *J. Chem. Phys.*, **37**, 1668 (1962).

[10] A. H. Nielsen, *ibid.*, **11**, 160 (1943).

[11] S. Reichman and J. Overend, *ibid.*, **47**, 3690 (1967).