

DOPPLER-FREE TWO-PHOTON SPECTRUM OF THE 0_0^0 BAND OF THE $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ TRANSITION IN DIFLUORODIAZIRINE, F_2CN_2

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The Doppler-free two-photon excitation spectrum of the vibrationless $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ transition of difluorodiazirine (F_2CN_2) has been recorded with a resolution of 15 MHz using a cw single-mode dye laser coupled to an external concentric resonator. The asymmetric rotor spectrum has been analysed and more than 350 lines randomly selected from all five branches were assigned in order to fit the ground- and excited-state rotational and quartic centrifugal distortion constants. From the rotational constants the r_{NN} and r_{FF} distances in the ground \tilde{X}^1A_1 and excited \tilde{A}^1B_1 state were determined. The geometry change upon excitation is found to be $\Delta r_{NN} = 3.89(2)$ pm and $\Delta r_{FF} = -4.09(2)$ pm. No perturbation in the rotational structure of the 0_0^0 band has been found. This points to a small singlet-triplet coupling matrix element in the small molecule limit.

1. Introduction

Since the molecule difluorodiazirine (DFD), F_2CN_2 , was reported for the first time [1] it has been the subject of a number of detailed investigations [2-6]. The aim of these investigations was to determine its geometric structure and to understand the spectral properties which are related to the dissociation into $:F_2C$ and N_2 when DFD is excited with UV light. Despite this dissociation DFD displays a well-structured spectrum of the $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ $n\pi^*$ transition (origin near 352 nm) which is symmetry allowed both in one- and two-photon excitation. The combined analysis of the vibrational spectrum [2,5] and the one- [4,7] and two-photon [8] electronic spectrum has yielded precise values of all nine fundamental vibrational frequencies in the ground \tilde{X}^1A_1 and excited \tilde{A}^1B_1 state.

The microwave spectrum of DFD is not yet available (presumably due to its small dipole moment [4,9,10]) and its ground-state geometry has only been estimated [7] from electron-diffraction studies of ref. [3]. Changes in the structure upon electronic excitation were determined from the contour analysis of the high-resolution Doppler-limited one-pho-

ton absorption spectrum [4,7]. A rotational contour spectrum of the 0_0^0 band in two-photon absorption measured with comparable resolution has been published in our recent work [8]. To resolve completely the rotational structure, sub-Doppler resolution is needed. A method to achieve this goal is Doppler-free two-photon excitation, recently established as a technique to provide rotational line spectra of large molecules, e.g., benzene [11,12]. The technique has now been applied to measure the two-photon spectrum of the 0_0^0 band of DFD. The analysis of the well-resolved line spectrum will be presented in this work and accurate rotational constants of *both* the ground *and* the excited electronic state of DFD will be reported. Some conclusions concerning the NN and FF distances and their change upon electronic excitation will be discussed.

2. Experimental setup

The experimental setup for cw Doppler-free two-photon spectroscopy of polyatomic molecules has been described in detail in our previous work [12]. Differing from our previous setup in ref. [12], the ultrahigh-resolution laser used in this work was an

Ar⁺-laser-pumped standing-wave single-mode dye laser (CR 599-21, Coherent). The dye used to work at 704 nm was pyridin 1. The output power of 100 mW from the dye laser was coupled into an external cavity with an input mirror of 90% reflectivity. This increases the power of the standing-wave light field for the Doppler-free two-photon excitation to 1.5 W and enhances the transition probability by nearly three orders of magnitude [12].

Scattered visible laser light was discriminated with optical filters (3 mm BG3 and 6 mm BG39, Schott) and single-fluorescence UV photons from two-photon-excited DFD were detected with a photomultiplier (56 DUVP, Valvo). The signal from the photomultiplier was fed into a window discriminator (Phillips Scientific model 6930) and counted for intervals of 20 ms corresponding to a change in the two-photon frequency of about 1 MHz during typical laser scans.

Relative frequency calibration was obtained from the simultaneous recording of the transmission signal from a stable 150 MHz confocal Fabry-Perot interferometer (CFT 500, Burleigh) used under mode-matching conditions. The absolute wavelength was

measured with an accuracy of 0.02 cm⁻¹ with a commercial wavemeter (WA 20, Burleigh).

The sample of DFD (0.9 Torr pressure) used for the measurement in this work is identical to the one used in our previous work [8] where the preparation is described in detail.

3. Experimental results

Overlapping laser scans of 13 GHz each were recorded to measure the complete rotational structure of the 0_g⁺ band with Doppler-free two-photon excitation. The resulting spectrum extends from -44 to +41 cm⁻¹ from the rotationless origin of the band and consists of well-separated rovibronic lines of 15 MHz width due to a measured pressure broadening of 10 MHz/Torr and the laser linewidth of about 3 MHz. The same spectral range has previously been measured with Doppler-limited resolution [8] and the result of the previous experiment is shown in the upper part of fig. 1. The rotational contour of the band consists of five branches with $\Delta J = -2, -1, 0, 1$ and 2 (O-, P-, Q-, R- and S-branch). On both sides

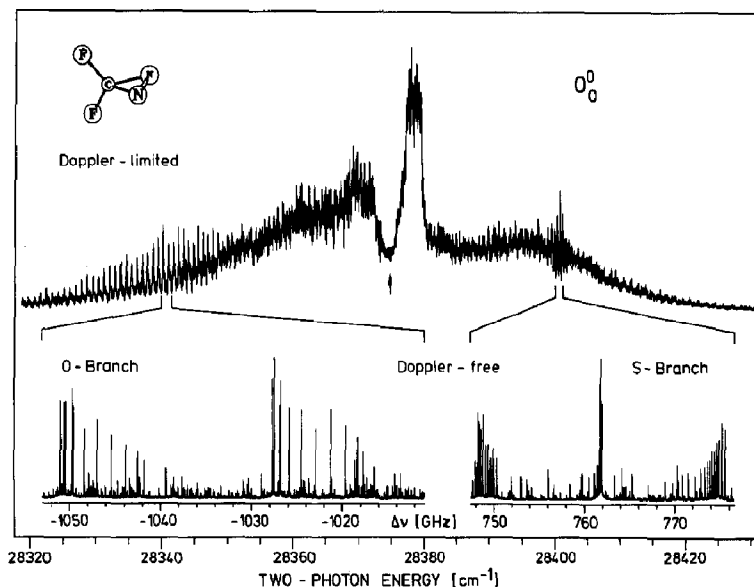


Fig. 1. Upper part: Doppler-limited two-photon spectrum of the 0_g⁺ band of difluorodiazirine (taken from ref. [8]). Energy scale bottom. Lower part: Parts of the Doppler-free two-photon spectrum. The energy scale for these parts is given relative to the rotationless origin at 28374.21(4) cm⁻¹ (marked by an arrow).

of the band, periodic features are seen which belong to the O-branch (red side) and to the S-branch (blue side). For both features part of the Doppler-free two-photon spectrum with resolved individual lines is shown in the lower part of fig. 1 on an extended frequency scale. Despite the fairly low output power of the standing-wave laser of about 100 mW an excellent signal to noise ratio is observed in the Doppler-free spectrum. The peak heights in the Doppler-limited spectrum are not only determined by the intensities but also by the density of the rotational lines, e.g., the dominant peak in the middle of the Doppler-limited spectrum is due to a high density of weak lines.

4. Rotational analysis

4.1. Line positions and selection rules

Difluorodiazirine is a highly asymmetric rotor molecule with C_{2v} symmetry in the ground and the excited electronic state [4]. For the computation of the rotational energy levels, Watson's A -reduced

Hamiltonian [13] in the I' representation was chosen. The levels are labelled by the quantum numbers J , K_a and K_c in the usual manner with the condition $K_a + K_c = J$ or $J + 1$. Due to the b_1 symmetry of the $B_1 \leftarrow A_1$ two-photon absorption only the following transitions between rotational states with $K_a K_c$ are possible: $ee \leftrightarrow oe$ or $eo \leftrightarrow oo$. e denotes K -even and o denotes K -odd. This differs from the one-photon spectrum, where the 0_0^0 band displays a B -type contour [4,7], i.e. $ee \leftrightarrow oo$ and $eo \leftrightarrow oe$ transitions are observed. This difference together with the additional O- and S-branch in the two-photon spectrum explains the differing contour of the 0_0^0 band in one- and two-photon spectroscopy [8].

4.2. Line intensities

The two-photon rotational line intensities of an asymmetric top molecule can be calculated as a weighted sum of rotational line intensities in the symmetric top basis [14,15]. For the 0_0^0 ($\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$) band of DFD under discussion the isotropic contribution to the two-photon transition probability vanishes because the band is not a totally

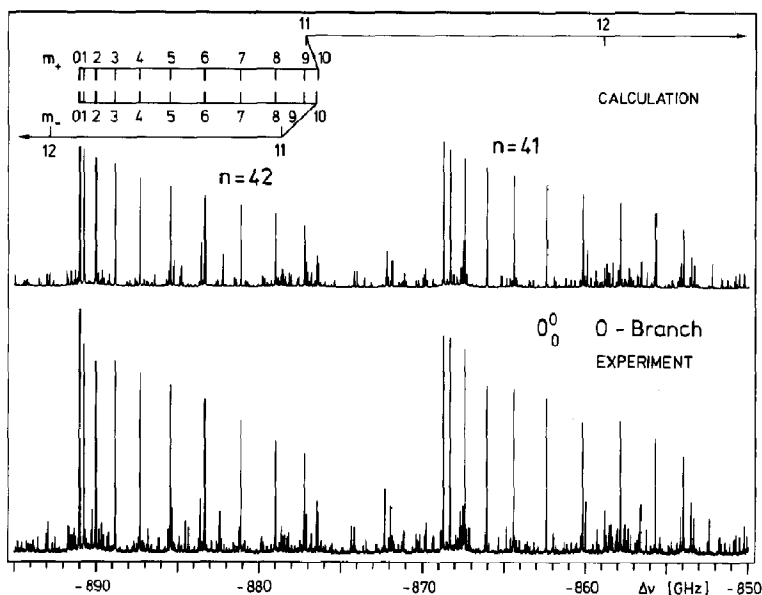


Fig. 2. Parts of the measured (lower trace) and calculated (upper trace) O-branch spectrum. For definition of m_{\pm} and n see text. The quantum numbers J' and K'_c of each line can be calculated by $J' = n - m_{\pm}$ and $K'_c = n - 2m_{\pm}$, $K'_a = m_-$ for transitions with $\Delta K_a = -1$ (lower assignments) and $K'_a = m_+ + 1$ for transitions with $\Delta K_a = +1$ (upper assignments).

symmetric transition and the antisymmetric anisotropic contribution vanishes because two photons of identical frequency are absorbed [15]. The remaining symmetric anisotropic contribution is described by the Placzek-Teller rotational factors and as a result the lines with the highest intensity are from $\Delta K_a = \pm 1$ and $\Delta K_c = 0, \pm 2$ transitions. Lines with $\Delta K_a = \pm 3$ and ± 5 , which are typically one or two orders of magnitude weaker, respectively, than corresponding ones with $\Delta K_a = \pm 1$, can also be found in the spectrum. The nuclear spin statistical weights for DFD are ee:eo:oe:oo = 15:15:21:21.

4.3. Assignment and fitting

With the previously best known set of rotational constants from Hepburn and Hollas [7] and the theoretically evaluated centrifugal distortion constants from Venkateswarlu [16], the expected rotational structure of the two-photon 0_0^0 band was calculated. This calculation helped to understand the organization of the band, especially the parts in the O- and the S-branch, with the periodic pattern (see fig. 1). As an example part of the periodic features of the O-branch around -29 cm^{-1} to the red of the rota-

tionless origin is shown in fig. 2 with the individual assignments (top), and compared with the experimental result (bottom).

The observed grouping is not due to the K -structure, but rather a grouping of lines with a constant value of $n = 2J' - K'_c$. These groups can be clearly identified from $n = 16$ to $n = 59$ to the red end of the recorded spectrum (see fig. 1). The distance between neighbouring groups is about 0.7 cm^{-1} and depends only weakly on the value of n . For each value of n the groups consist of a series of ^{16}O transitions and a series of ^{18}O transitions. These transitions are labelled with m_{-1} ($\Delta K_a = -1$) and m_{+1} ($\Delta K_a = +1$). $m_{\pm 1}$ is given by $m_{\pm 1} = J' - K'_c$. From fig. 2 it can be seen that the two series coincide up to fairly high values of m_{-1} and m_{+1} since the asymmetry splitting is negligible for the corresponding high values of K_c . First the asymmetry splitting in the $\tilde{A} \ ^1B_1$ and shortly after in the $\tilde{X} \ ^1A_1$ state becomes noticeable and this gives rise to the peculiar positioning of the lines shown in fig. 2.

From the initial calculation it was estimated that the periodic feature on the left side of fig. 2 should belong to $n = 42$. Several peaks in the periodic feature of the O-branch were assigned accordingly and

Table 1

Rotational and quartic centrifugal distortion constants (cm^{-1}) of difluorodiazirine for the vibrationless ground $\tilde{X} \ ^1A_1$ and the excited $\tilde{A} \ ^1B_1$ state. Standard deviations of the constants are given in parentheses as uncertainties in the last digit, while the overall error is estimated to be one order of magnitude higher. σ is the standard deviation of the fit (cm^{-1})

	1A_1	1B_1
A_0	0.297846(3)	0.303087(3)
B_0	0.220672(1)	0.211007(1)
C_0	0.1527547(4)	0.1512282(4)
κ	-0.0638	-0.2127
ν_{00}		28374.21(4)
$10^6 \Delta_J$	0.0558 ^{a)}	0.0573(1)
$10^6 \Delta_{JK}$	0.1298 ^{a)}	0.147(2)
$10^6 \Delta_K$	0.0456 ^{a)}	-0.009(9)
$10^6 \delta_J$	0.0173 ^{a)}	0.0173 ^{b)}
$10^6 \delta_K$	0.074 ^{a)}	0.074 ^{b)}
ΔA		0.005241(6)
ΔB		-0.009665(2)
ΔC		-0.0015265(8)
σ		0.00021

^{a)} Values calculated from theoretical results [16] with the rotational constants of ref. [7] according to standard formulas [18].

^{b)} Held constant during fit.

used as input for a least-squares-fit FORTRAN program written by Jones and Typke [17] for microwave and infrared spectra and adapted to the two-photon spectrum by us. Comparison of the simulated spectrum calculated with the resulting new set of rotational constants with the measured spectrum confirmed the particular choice of the value of n . In addition, the calculated and the observed spectrum were also compared for the periodic feature of the S-branch. In this branch each group of lines consists of ^{32}S and ^{34}S transitions with constant J' while the strongest line corresponds to $K'_c = J'$. For low values of J' a red-shading of each structure is observed which turns into a blue-shading for high values of J' at $J' = 48$. This turnover depends very critically on the rotational constants and was therefore used to check the correctness of the preliminary fit.

With the predictions from the preliminary fit, more than 350 lines were assigned from all five branches of the spectrum and a final fit to these assignments yielded the rotational and centrifugal distortion constants shown in table 1. We were able to determine the constants of the \tilde{X}^1A_1 and \tilde{A}^1B_1 state, while in previous investigations [3,4,7] the constants of the \tilde{X}^1A_1 state had to be determined from geometric

considerations. The changes in the rotational constants upon electronic excitation do not deviate strongly from the previous values [4,7], while the constants themselves do. The preciseness of the final fit is demonstrated in figs. 2 and 3, where parts of the calculated O-branch spectrum and S-branch spectrum, respectively, are compared with the measured spectrum. In particular, the sensitive turnover in the S-branch is well reproduced (see fig. 3).

For the C_{2v} symmetry of DFD the rotational constants A , B and C are related [4,7] to the N-N distance r_{NN} by

$$m_{\text{N}} r_{\text{NN}}^2 = (A^{-1} + B^{-1} - C^{-1}) h / 8\pi^2 c \quad (1)$$

and the nonbonding F-F distance r_{FF} by

$$m_{\text{F}} r_{\text{FF}}^2 = (A^{-1} - B^{-1} + C^{-1}) h / 8\pi^2 c. \quad (2)$$

Here m_{N} and m_{F} are the masses of the nitrogen and fluorine atoms, respectively. This means that two geometric parameters can be determined purely from the spectrum of one isotope. It should be noted that only the apparent bond length r_0 can be derived from the rotational constants A_0 , B_0 , and C_0 and not the equilibrium distances r_e . The results are listed in table 2. The values $(r_{\text{FF}}'')_0$ and $(r_{\text{NN}}'')_0$ for the \tilde{X}^1A_1

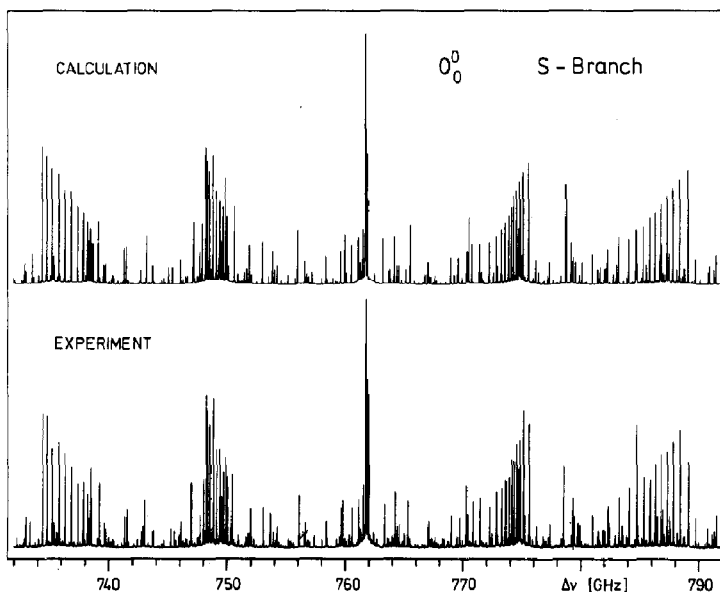


Fig. 3. Part of the measured (lower trace) and calculated (upper trace) S-branch spectrum, where the turning of the periodic pattern occurs (see text).

Table 2

Apparent length ($r_{\text{NN}})_0$ of the NN-bond and the distance ($r_{\text{FF}})_0$ of difluorodiazirine and their changes upon excitation (pm). The values were calculated from the constants given in table 1 according to eqs. (1) and (2)

	1A_1	1B_1	Δ
$(r_{\text{NN}})_0$	127.15(1)	131.04(1)	3.89(2)
$(r_{\text{FF}})_0$	218.32(1)	214.23(1)	-4.09(2)

state are similar to the values obtained from electron diffraction [3]. The values Δr_{FF} and Δr_{NN} for the changes of the distances from the \tilde{X}^1A_1 to the \tilde{A}^1B_1 state are similar to the values obtained from the contour fit to the one-photon spectrum by Hepburn et al. [7], while the value of Δr_{NN} differs from that obtained by Lombardi et al. [4].

5. Summary and conclusions

In this work the Doppler-free two-photon excitation spectrum of the vibrationless $\tilde{A}^1B_1 \leftarrow \tilde{X}^1A_1$ $n\pi^*$ transition of the asymmetric rotor molecule difluorodiazirine, F_2CN_2 , has been measured and analysed. We assigned more than 350 lines and determined the rotational constants of both electronic states, \tilde{X}^1A_1 and \tilde{A}^1B_1 and most of the quartic centrifugal distortion constants. From these values the N-N distance r_{NN} and the nonbonding F-F distance r_{FF} was determined.

There is a close agreement of calculated and experimental line positions for all 364 assigned lines, which were randomly selected from the rotational contour. The standard deviation of the fit is very small and no shifts of lines are found within the experimental accuracy. From this we conclude that no significant perturbation of the rotational line structure is present at all in the 0_0^0 band.

Generally, two sources for rotational perturbations could exist at zero excess energy in the \tilde{A}^1B_1 state. These are interactions of the 0^0 level with highly vibrational states either in the triplet 3B_1 or the \tilde{X}^1A_1 ground electronic state. For an excitation energy of 28374 cm^{-1} we calculate a total density of vibrational states in the \tilde{X}^1A_1 state of $2.25 \times 10^5 / \text{cm}^{-1}$ or 7.5 states per MHz. For such a high density of states no isolated perturbations with detectable

shifts of more than 20 MHz are expected. According to previous calculations [4,19], the lowest triplet state 3B_1 is located around 7200 cm^{-1} below the vibrationless \tilde{A}^1B_1 state. For this excess energy a total density of states of $150 / \text{cm}^{-1}$ or one state every 200 MHz is estimated. This low density of states could lead to isolated perturbations. For similar densities in the triplet state perturbations have indeed been observed in pyrazine [20,21], pyrimidine [22] and butynal [23]. Since no perturbations are detected in the present case we conclude that in difluorodiazirine the average coupling matrix element for singlet-triplet coupling is considerably smaller than the average distance of triplet states ($V \ll 1/\rho$). The singlet-triplet coupling is in the small-molecule limit and singlet-triplet mixing plays no dominant role in the 0^0 level of difluorodiazirine. Difluorodiazirine is known to predissociate slowly even in the 0^0 level of the \tilde{A}^1B_1 state [6]. From the results of this work we conclude that the nonradiative decay preceding the dissociation is expected to be internal conversion rather than intersystem crossing. This may be different at higher excess energy where the density of triplet states increases and Franck-Condon factors may become more favourable.

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