Infrared-Microwave Double Resonance and Double Photon Transitions in FCN*

Harold Jones

Department of Chemistry, University of Ulm, Welt Germany

(Z. Naturforsch. **31 a**, 1614–1619 [1976]; received November 12, 1976)

The utility of a conventional microwave spectrometer in determining the relative disposition of a CO_2-laser line and a molecular transition and ultimately the exact frequency of an infrared transition, is demonstrated by making use of three non-linear spectroscopic effects, high frequency Stark effect, IR-MW double resonance and IR-MW double photon transitions. New situations are encountered in the production of the double photon transitions and the observation of the high frequency Stark effect. From a combination of the double photon transitions with double resonance signals produced in single d. c. Stark components it was concluded that the R(2) transition of the ν_1 band of the linear molecule FCN lies 104 ± 15 MHz lower in frequency than the R(20), 9.4 μm CO_2-laser line i.e. R(2) transition $= 1079.5871 \pm 0.0005$ cm^{-1}.

Introduction

To produce strong double resonance signals with a fixed frequency laser, a laser line must fall within the Doppler width of a molecular transition. Quite a number of studies relying on such accidental coincidences have already been reported e. g. [1–7].

However weak double resonance signals may also be produced by off-resonant pumping effects even when the laser line lies considerably outside the Doppler width of a molecular transition. Under these circumstances and especially if the frequency mismatch is small the possibility arises of several other types of phenomena being observed. In this paper we wish to report the identification and investigation of such a relationship between the 9.4 μm, R(20) CO_2 laser line and the R(2) transition of the ν_1 band (C-F stretch) of FCN. In a conventional infrared study of the ν_1 band of FCN by Cole et al. [8] the R(2) transition was report at 1078.59 ± 0.05 cm^{-1}. Consequently this transition was expected to lie near the R(20) CO_2 laser line at 1078.59064 cm^{-1} (Ref. [9]). In the present study it has been shown that the degree of coincidence between the R(20) laser line and the R(2) transition is much better than the error limits of ± 0.05 cm^{-1} (~ 1500 MHz) of the conventional measurement. From a combination of three different types of information enumerated below, it has been conclusively shown that the R(20) laser line lies approximately 104 MHz higher in frequency than the R(2) transition.

a) The double resonance signals were observed to be shifted slightly from the frequencies of the associated rotational transitions. This effect was interpreted as being produced by a high frequency Stark effect [10–12].

b) Broad "double resonance" signals were observed at frequencies where there were no rotational transitions. These signals were interpreted as being produced by infrared-microwave double photon transitions of the type with an intermediate level [13–15].

c) A d.c. electric field was applied to the sample of FCN and two Stark components of the R(2) transition were tuned into resonance with the laser line. Resonance was indicated by a very large increase in the intensity of the double resonance signals produced at the frequencies of rotational transition Stark components.

Experimental

All observations were made using the microwave radiation as signal field and the infrared radiation as pumping field. The unstabilised CO_2 laser used produced 8 Watts output on the R(20) line. The laser output was chopped at a frequency of 1 KHz and phase-sensitive detection at this frequency was employed. Microwave power of 150 mWatts at 63 GHz and 200 mWatts at 42 GHz was produced by OKI 60V12 and 45V11 klystrons, which could be operated in either free-run or phase-locked modes. Two different waveguide cells were used for the measurements, one a 2 metre X-band Stark cell, the other a 60 cm length of K-band waveguide. For the

* This work is supported by the Deutsche Forschungsgemeinschaft under the title "Infrarot-Mikrowellen-Doppelresonanz im Bereich der Molekülspektroskopie".
Reprint requests to Dr. Harold Jones, Abt. Physikalische Chemie, Universität Ulm, Oberer Eselsberg, *D-7900 Ulm*.

Stark component measurements the Stark cell was calibrated using OCS with an assumed dipole moment of 0.71521 D [16]. FCN was produced by pyrolysis of cyanuric fluoride [17].

Observations and Discussion

Relatively weak double resonance signals were observed in the ground state $J=1\rightarrow 2$ and $J=2\rightarrow 3$ transitions and in the $v_1=1$ excited state $J=2'\rightarrow 3'$ transition (primed quantum numbers always refer to the excited state) close to the frequencies predicted for these transitions from the measurements of Lafferty and Lide [18] (Table 1). The $J=1\rightarrow 2$

Table 1.

Transition	Microwave Signal [MHz]	Double Resonance [MHz]	Double Photon [MHz]	$\Delta\omega$ [MHz]
$J=1\rightarrow 2$	42 216.9	42 217.2	42 126	91
$J=2\rightarrow 3$	63 325.1	63 325.5	63 433	108
$J=2'\rightarrow 3'$	63 065.0	63 064.9	63 160	95

double resonance signal corresponded to an increase in microwave absorption in the presence of laser radiation and both $J=2\rightarrow 3$ transitions corresponded to a decrease in microwave absorption. This is completely in keeping with the laser transfering population from the ground $J=2$ level into the $v_1=1$, $J=3$ level (i. e. the R(2) infrared transition was partially pumped) Figure 1(a). From the smallness of the microwave absorption changes produced

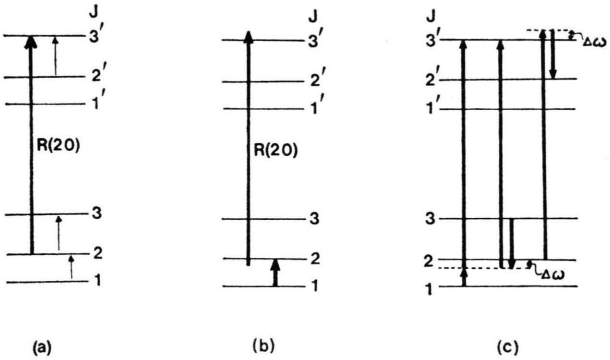

Fig. 1. Energy level scheme of the ground and $v_1=1$ excited states of FCN. (c) Three microwave transitions (thin arrows) observed to produce double resonance signals with the $R(20)$ laser line (thick arrow). (b) Disposition of levels in Equation (1). (c) Three infrared-microwave double photon transitions observed left to right $J=1\rightarrow\rightarrow 3'$, $J=3\rightarrow\rightarrow 3'$ and $J=2\rightarrow\rightarrow 2'$.

by the laser radiation, ~5% for the $v_1=1$ transition and $\leqslant 1\%$ for the ground state transitions, it was clear that the laser line was considerably off-resonant with the R(2) transition. Moreover the relatively small change in double resonance signal strength produced by tuning the laser within its gain profile (~ ±25 MHz) showed that this range did not overlap to any great extent with the Doppler broadened R(2) transition. The relative positioning and the frequency separation between the R(20) laser line and the R(2) transition were determined from the three additional types of information.

a) High frequency Stark effect

The double resonance signals were observed to be slightly shifted from the centre frequency of the associated rotational transitions (Table 1) and to be considerably asymmetric. The signals observed for the ground state $J=1\rightarrow 2$ and $J=2\rightarrow 3$ transitions are shown in Figures 2(a) and 2(c). Both the asymmetry and the frequency shift may be explained as being produced by a laser-induced high frequency Stark effect similar to that observed by Lemaire et al. [12] in ammonia.

Considering the situation where the R(20) laser line of frequency ω_l is slightly off-resonant with the infrared transition $J=2\rightarrow 3'$ of frequency $\omega_{3',2}$ (Fig. 1(b)) using expressions given in Ref. [12] the shift in the ground state $J=1\rightarrow 2$ rotational transition is

$$\delta\omega_{2,1} = -E^2/\hbar\cdot|\mu_{3',2}|^2\,\omega_{3',2}/(\omega_{3',2}^2-\omega_l^2) \qquad (1)$$

where E is the laser field strength and $\mu_{3',2}$ is the transition moment for the $J=2\rightarrow 3'$ transition. From this expression it can be seen that when $\omega_l>\omega_{3',2}$, $\delta\omega_{2,1}$ is positive and when $\omega_l<\omega_{3',2}$, $\delta\omega_{2,1}$ is negative. For the ground state $J=2\rightarrow 3$ transition the situation is reversed.

The main difference between this case and those in Ref. [12] was that here the laser induced not only a shift in frequency but also a change in intensity. For the correct interpretation of these signals both of these effects had to be considered. This is illustrated in Figures 2(b) and 2(d). To reproduce the observed signals the only possability was that the $J=1\rightarrow 2$ transition was shifted towards high frequency and the $J=2\rightarrow 3$ transition towards low frequency. From the above considerations this means that the R(20) line lies to the high frequency side of the R(2) transition (i. e. $\omega_l>\omega_{3',2}$).

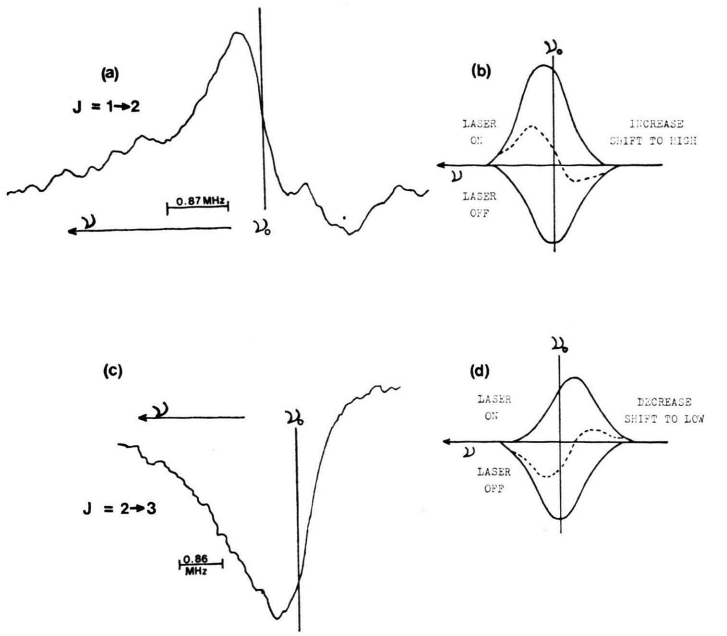

Fig. 2. (a) and (c) double resonance signals observed for the ground state $J=1\rightarrow 2$ and $J=2\rightarrow 3$ transitions. ν_0 represents the centre of the unperturbed rotational transition. (b) and (d) diagramatic explanation of the production of the line shapes of (a) and (c). The full lines represent the actual microwave absorption lines in presence and absence of laser radiation, the broken line represents the sum of these two and hence the observed signal.

b) Double photon transitions

This conclusion was strongly supported by the observation of three broad signals (~ 50 MHz wide) centred approximately 100 MHz below the ground state $J=1\rightarrow 2$ transition and about 100 MHz above both the ground and excited state $J=2\rightarrow 3$ transitions (Table 1). The three double photon transitions responsible for the production of these signals are shown in Figure 1(c). They correspond to transitions $J=1\rightarrow\rightarrow 3'$, $J=3\rightarrow\rightarrow 3'$ and $J=2\rightarrow\rightarrow 2'$. The moment for the $J=1\rightarrow\rightarrow 3'$ transition is given [15] by

$$(\mu E)_{1\rightarrow\rightarrow 3'} = \frac{\langle 1 \mid \mu_p E_m \mid 2 \rangle \langle 2 \mid \mu_v E_l \mid 3' \rangle}{2\, h\, \Delta\omega} \quad (2)$$

where μ_p is the permanent dipole moment, μ_v the vibrational transition moment, E_m and E_l the microwave and laser field strengths respectively and $\Delta\omega$ the frequency mismatch between the R(20) laser line and the R(2) transition. From this expression it is apparent that double photon transitions are favoured when μ_p, μ_v, E_m and E_l are large and when $\Delta\omega$ is small. The present case was extremely favourable for the observation of double photon transitions, both μ_p and μ_v were large, $\Delta\omega$ was only ~ 100 MHz, and reasonably high laser and microwave power levels were available. The signals observed in the region of the ground state $J=2\rightarrow 3$ rotational transition are shown in Figure 3.

The broad double photon signals had the following characteristics; i) only observable in the presence of infared radiation, ii) only observable in the presence of gas, iii) increased in intensity with increasing microwave power (diode current kept constant), iv) relatively stronger in the small sectioned K-band cell than in the X-band cell (i. e. both infrared and microwave power densities higher), v) frequency off-set from double resonance was variable between 80 and 120 MHz dependent on the laser frequency, vi) polarity of the signal was the same as the nearby double resonance signal.

These characteristics fulfill those expected for double photon transitions indicated by Eq. (2) and Figure 1 (c). The broadness of these signals is explainable by the fact that although they were observed in the microwave region, they correspond to infrared transitions and would be expected to display a large Doppler width (Doppler half-width for FCN ~ 30 MHz). As may be seen from consideration of Fig. 1(c) if the laser frequency was ~ 100 MHz above that of the R(2) transition (i. e. $\Delta\omega \approx 100$ MHz) the double photon transition $J=1\rightarrow\rightarrow 3'$ would be expected to appear as a microwave absorption ~ 100 MHz below the ground state $J=1\rightarrow 2$ transition as was observed. Also, in ac-

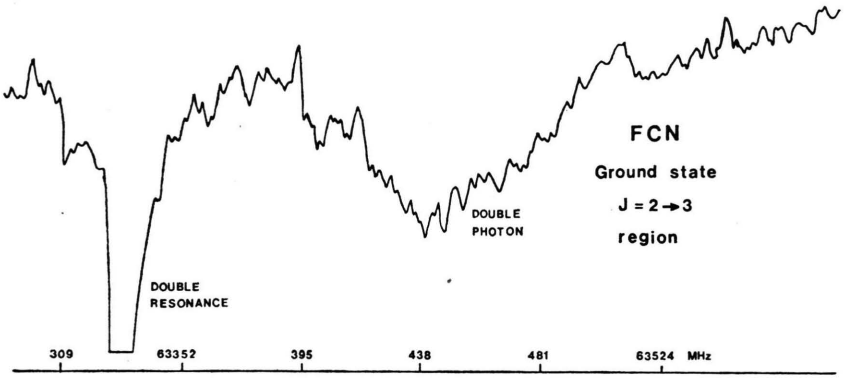

Fig. 3. Signals observed in the $J=2\rightarrow 3$ ground state region with 8 Watts $R(20)$ laser radiation present. The narrow feature is the double resonance signal (goes off-scale) and the broad feature is the double photon transition.

cordance with observation, the transitions $J = 3 \rightarrow\rightarrow 3'$ and $J = 2 \rightarrow\rightarrow 2'$ would be expected to produce signals corresponding to stimulated emission of microwaves ~ 100 MHz above the frequencies of the $J = 2 \rightarrow 3$ ground and excited state rotational transitions.

The accuracy to which $\Delta\omega$ could be determined from these measurements was limited by two factors. The broad line-widths made location of the centre of the signal relatively inaccurate, especially since considerable line shape distortion was observed. The second source of error was the frequency instability of the unstabilised laser used in this work. The frequencies given in Table 1 for the double photon transitions represent the average of several measurements where in each case the laser was tuned to near the centre of its gain profile. All measurements gave a value of $\Delta\omega$ within ± 15 MHz of the average value of 98 MHz.

In all previous studies of this type of double photon transition [13–15], the infrared radiation was monitored. This experimental arrangement is theoretically more sensitive than that used in the present work, since the higher energy photon is detected. To the author's knowledge this is the first time that infrared-microwave double photon transitions have been observed using the microwave field as signal. The significance of this is that it shows that given favourable circumstances these processes are strong enough to be easily detected.

Stark component double resonance signals

The conclusion that the R(20) laser line lay approximately 100 MHz above the R(2) transition was confirmed by tuning two Stark components of this infrared transition into resonance with the laser by application of a d.c. electric field. The required shift was small enough to allow this to be done in a waveguide Stark cell of conventional design. Resonance with the laser line was indicated by large (factor 50 – 100) increase in the intensity of the double resonance signals of connected rotational transition Stark components.

The second order energy shift produced in the levels of a linear molecule by an electric field ε, is given by

$$\Delta E = u^2 \varepsilon^2 / 2\,h\,B \cdot [J(J+1) - 3\,M^2] / J(J+1)\,(2\,J-1)\,(2\,J+3)\,. \quad (3)$$

From this expression the frequency shifts of rotational transitions within a particular vibrational state and that of infrared transitions between the ground and $v_1 = 1$ states were evaluated.

Within the waveguide cell the electric vector of the microwave radiation was parallel to the applied electric field and as a consequence of this in all cases only microwave transitions obeying the selection rule $\Delta M = 0$ were observed. The plane of polarisation of the laser radiation could be rotated so that either parallel or perpendicular configurations could be produced. Thus infrared Stark components corresponding to transitions obeying either $\Delta M = \pm 1$ or $\Delta M = 0$ could be pumped. The energy level scheme is shown in Figure 4.

To attain resonance with the R(20) laser line it was necessary for a Stark component of the R(2) infrared transition to move to higher frequency with increasing electric field. With the perpendicular configuration the Stark component which moved fastest towards higher frequency corresponded to the infrared transition $J, M = 2, 2 \rightarrow 3', 1'$. As this transition approached resonance with the laser line

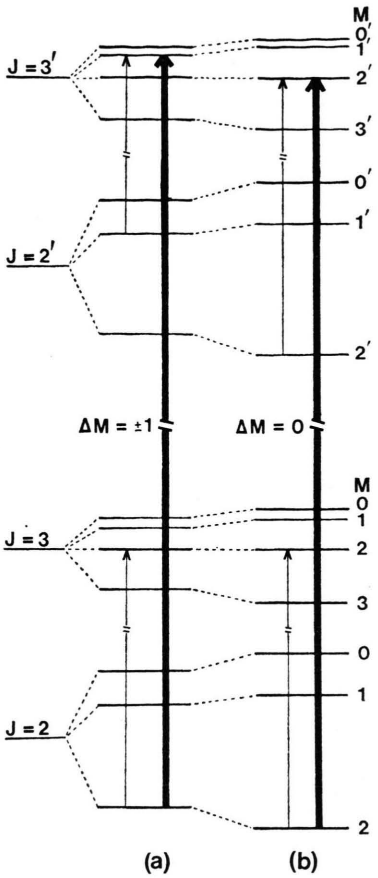

Fig. 4. Representation of the Stark splittings produced by application of a d.c. electric field. (a) Field = 5680 V/cm, plane of polarisation of laser output perpendicular to the field. The infrared transition $J, M = 2,2 \rightarrow 3',1'$ resonates with the $R(20)$ laser line thus producing strong double resonance signals in the ground state $J, M = 2,2 \rightarrow 3,2$ and excited state $J, M = 2',1' \rightarrow 3',1'$ rotational transitions. (b) Field = 6490 V/cm, plane of polarisation of laser parallel to field. The infrared transition $J, M = 2,2 \rightarrow 3',2'$ resonates with the laser line producing strong signals in the ground and excited state $J, M = 2,2 \rightarrow 3,2$ transitions.

the double resonance signals produced in the ground state $J, M = 2, 2 \rightarrow 3, 2$ and the excited state $J, M = 2', 1' \rightarrow 3', 1'$ microwave Stark components were observed to increase strongly in intensity (Figure 4(a)). These signals reached a maximum when the infrared Stark component coincided with the laser line. Since the Doppler half-width for the infrared transition was ~ 30 MHz a broad maximum in signal intensity was observed centred at a field strength of approximately 5680 V/cm. From measurements of the Stark shifts produced in the

Table 2. Stark Shifts [MHz], * = $\Delta\omega$.

Laser Perpendicular 5680 V/cm		
Transition	Observed	Calculated
$J, M = 2,2 \rightarrow 3,2$	+ 85.3	+ 85.0
$J, M = 2',1' \rightarrow 3',1'$	− 11.4	− 12.7
$J, M = 2,2 \rightarrow 3',1'$		+114.7 *

Laser Parallel 6490 V/cm		
Transition	Observed	Calculated
$J, M = 2,2 \rightarrow 3,2$	+112.3	+111.1
$J, M = 2',2 \rightarrow 3',2'$	+110.1	+111.5
$J, M = 2,2 \rightarrow 3',2'$		+111.1 *

rotational transitions it was calculated that the $J, M = 2, 2 \rightarrow 3', 1'$ infrared Stark component lay ~ 115 MHz above the unperturbed R(2) infrared transition at this field strength, i. e. $\Delta\omega = \sim 115$ MHz (Table 2).

With the plane of polarisation of the laser radiation parallel to the Stark field the infrared Stark component which moved fasted towards the laser line corresponded to $J, M = 2, 2 \rightarrow 3', 2'$. In this case increases in the double resonance signals produced by the ground state $J, M = 2, 2 \rightarrow 3, 2$ and the excited state $J, M = 2', 2' \rightarrow 3', 2'$ microwave Stark components were observed. Maximum signal was observed at a field of approximately 6490 V/cm, which corresponded to a frequency shift of the $J, M = 2, 2 \rightarrow 3', 2'$ infrared Stark component of approximately 111 MHz, i. e. $\omega\Delta = \sim 111$ MHz (Table 2).

The microwave Stark effect data (Table 2) was adequately fit with a dipole moment for FCN of 2.15 ± 0.05 Debye in both ground and excited states. This dipole moment is insignificantly different from the 2.17 ± 0.05 Debye measured by Tyler and Sheridan [19] for the ground state of FCN. The accuracy to which the separation of the laser line and the R(2) transition was determined from these measurements was limited by three factors. As before the laser stability had a direct influence and the poor field homogenity possible in a waveguide cell limited the accuracy of the frequency measurements of the Stark shifts. Since the infrared Stark components had a Doppler width of ~ 30 MHz the intensity maximum was necessarily broad and the centre was difficult to locate. Consequently although the two values of $\Delta\omega$ determined for the two infrared Stark components agree closely it is unlikely that the absolute accuracy is better than for the double photon transitions.

The average value of $\Delta\omega$ from both double photon and Stark effect measurements was 104 ± 15 MHz. Thus the R(2) infrared transition lies at 1079.5871 ± 0.0005 cm^{-1}. Since the rotational constants for both ground and $v_1 = 1$ excited state are known[18] this measurement enables all transitions of the ν_1 band to be calculated to an accuracy of at least 0.001 cm^{-1}.

The precision of the frequency measurements carried out in this work can be greatly improved by increased sophistication of the laser utilised and resort to double photon[14] and Stark laser spectroscopy[20, 21] Lamb-dip techniques.

Acknowledgements

The author wishes to thank Professor H. D. Rudolph for his support and encouragement in this work and to thank Michael Römheld and Franz Kohler for critical reading of the manuscript and many discussions on the subject matter.

1 T. Shimizu and T. Oka, Phys. Rev. A **2**, 1177 [1970].
2 L. Frenkel, H. Marantz, and T. ullivan, Phys. Rev. A **3**, 1630 [1971].
3 J. Lemaire, J. Thibault, F. Herlemont, and J. Houriez, Mol. Phys. **27**, 611 [1974].
4 W. A. Kreiner, A. Eyer, and H. Jones, J. Mol. Spectrosc. **52**, 420 [1970].
5 H. Jones and F. Kohler, J. Mol. Spectrosc. **58**, 125 [1975].
6 W. A. Kreiner and T. Oka, Can. J. Phys. **53**, 2000 [1975].
7 H. Jones, F. Kohler, and H. D. Rudolph, J. Mol. Spectrosc. **63**, 205 [1976].
8 A. R. H. Cole, L. Isaacson, and R. C. Lord, J. Mol. Spectrosc. **23**, 86 [1967].
9 F. R. Peterson, D. G. McDonald, J. D. Cupp, and B. L. Danielson, Phys. Rev. Letts. **31**, 573 [1973].
10 S. H. Autler and C. H. Townes, Phys. Rev. **100**, 703 [1955].
11 P. Glorieux, J. Legrand, B. Macke, and J. Messelyn, J. Quant. Spectrosc. Radiat. Trans. **12**, 731 [1972].
12 J. Lemaire, J. Houriez, and F. Herlemont, J. Quant. Spectrosc. Radiat. Trans. **13**, 923 [1973].
13 T. Oka and T. Shimizu, Appl. Phys. Letts. **19**, 88 [1971].
14 S. M. Freund and T. Oka, Appl. Phys. Letts. **21**, 60 [1972].
15 T. Oka, Laser Spectroscopy, Edit. R. Brewer and A. Mooradian, Plenum Pub. Corp., New York 1974.
16 J. S. Muenter, J. Chem. Phys. **48**, 4544 [1968].
17 F. S. Fawcett and R. D. Lipscount, J. Amer. Chem. Soc. **86**, 2576 [1964]
18 W. J. Lafferty and D. R. Lide, J. Mol. Spectrosc. **23**, 94 [1967].
19 J. K. Tyler and J. Sheridan, Trans. Faraday Soc. **59**, 2661 [1963].
20 S. M. Freund, G. Duxbury, M. Römheld, J. T. Tiedje, and T. Oka, J. Mol. Spectrosc. **52**, 38 [1974].
21 J. W. C. Johns, A. R. W. McKellar, and A. Trombetti, J. Mol. Spectrosc. **55**, 131 [1975].