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VIBRATIONAL FUNDAMENTALS OF CF_2N_2 FROM THE ULTRAVIOLET ABSORPTION SPECTRUM

by

J. D. Simmons, I. R. Bartky and A. M. Bass

Technical Report

to

National Aeronautics and Space Administration
Washington, D. C.

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

[redacted]

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Preface

A manuscript based upon this report will be submitted for publication as a Letter to the Editor in the Journal of Molecular Spectroscopy.

VIBRATIONAL FUNDAMENTALS OF CF_2N_2 FROM THE ULTRAVIOLET ABSORPTION SPECTRUM[*]

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J. D. Simmons[**], I. R. Bartky and A. M. Bass

Abstract

The ultraviolet absorption spectrum of CF_2N_2 has been observed and found to include bands of two types. All of the bands of one type can be analyzed in terms of four totally symmetric vibrational frequencies plus a prominent sequence of difference bands. Some bands of the second type can be interpreted as vibronically allowed fundamentals induced by the nontotally symmetric torsional vibration. This latter assignment reveals enough information to account for the difference bands of the first type. All ground state fundamental assignments are compatible with earlier infrared and Raman results.

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[**] National Academy of Sciences-National Research Council Postdoctoral Research Associate at the National Bureau of Standards.

CF_2N_2 has recently been prepared and characterized by Mitsch (1). The infrared and Raman spectra have been observed and interpreted in terms of a cyclic diazirine structure as opposed to the isomeric linear diazomethane structure (2). The following preliminary vibrational analysis of the electronic spectrum is offered as further support for that assignment.

The ultraviolet absorption spectrum has been observed in the 3750-3000 Å region under high resolution and with sufficient path-lengths, using a multiple reflection cell, to observe the vibronically allowed ground state fundamentals. The system contains bands of at least two distinct types; a strong group of broad bands with three intensity maxima and a much weaker group with one prominent sharp maximum.

On the basis of a cyclic difluorodiazirine with C_{2v} symmetry, there are four totally symmetric vibrations of species A_1, and five nontotally symmetric vibrations - one, two and two of species A_2, B_1 and B_2, respectively. Vibronic selection rules allow only totally symmetric fundamental and combination frequencies to appear in the electronic spectrum with the same band-type as the origin band. Any nontotally symmetric fundamental which appears with appreciable intensity due to vibronic interaction must have a band-type different from that of the origin.

All of the broad-type bands can easily be interpreted in terms of four totally symmetric vibrational frequencies accompanied by a strong sequence of difference bands with the origin at 28374.6 cm^{-1}. The assignment for these totally symmetric vibrations is summarized in Table I where the results from the ultraviolet data are compared with those from Ref. 2. The agreement for the ground state fundamentals is very good except for ν_3. Here, although the deviation between the infrared and the ultraviolet data is uncomfortably large, the assignment in each case is rather convincing.

The relative intensities of the upper state progressions, in decreasing order, are ν_1 (4 members), ν_4 (2 members), ν_3 (1 member) and ν_2. While the ground state ν_2 fundamental appears in the long-path experiments, it has much less intensity than does ν_1, even though it has a more favorable Boltzmann distribution. The ν_2 upper state fundamental is not observed and is presumably overlapped by stronger bands in the expected region. Since ν_1 and ν_4 may be described as the symmetric NN stretch and symmetric CF_2 deformation respectively, one would conclude from Franck-Condon considerations that the most significant change in geometry between the two electronic states is a stretching of the nitrogen-nitrogen bond which expands the ring and effects some change in the FCF angle.

It should also be noted that the nontotally symmetric ν_6 torsional vibration (species A_2) which has a Raman active frequency of 451 cm^{-1} (2) also appears in the electronic spectrum by vibronic interaction. As expected from the selection rules, the ground and upper state fundamentals -- with frequencies of 448 cm^{-1} and 327 cm^{-1}, respectively, from the broad-type origin -- are bands of the sharp type. This low frequency vibration offers a convincing assignment for the above mentioned strong sequence of broad-type difference bands which has a 120.6 cm^{-1} interval.

The ν_5 assignment does not, however, account for all of the sharp bands observed. There is preliminary evidence for another transition in this region. Further work on this system is in progress including an attempt to analyze the partially resolved rotational structure by an asymmetric rotor contour technique.

The authors are grateful to Dr. Ronald Mitsch of the Minnesota Mining and Manufacturing Company for supplying the sample and to Dr. Norman Craig for making a preprint of Ref. 2 available in advance of publication.

REFERENCES

(1). Ronald A. Mitsch, J. Heterocyclic Chem. 1, 59 (1964).

(2). C. W. Bjork, N. C. Craig, R. A. Mitsch and J. Overend, J. Am. Chem. Soc. (in press).

Table I. Vibrational Assignment for the A_1 Species in CF_2N_2

Vibration	IR (vapor) Ref. 2 (cm^{-1})	Raman (liq.) Ref. 2 (cm^{-1})	Ultraviolet (vapor) This work v'' (cm^{-1})	v' (cm^{-1})
ν_1	1563	1560	1564.0	1436.9
ν_2	1282	1280	1282.9	----
ν_3	805	804	775.0	643.3
ν_4	502	500	500.2	516.6