NATIONAL BUREAU OF STANDARDS REPORT

R-64

9008

AN ELECTRIC QUADRUPOLE TRANSITION IN THE $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$ SYSTEM OF CO

by

S. G. Tilford and J. D. Simmons

Technical Report

to

National Aeronautics and Space Administration

Washington, D. C.

GPO PRICE $ ________

CFSTI PRICE(S) $ ________

Hard copy (HC) $1.00

Microfiche (MF) .50

ff 653 July 65

N66-16698
(ACCESSION NUMBER)
(THRU)
20
(PAGES)
1
(CODE)
CR 70045
(NASA CR OR TMX OR AD NUMBER)
24
(CATEGORY)
FACILITY FORM 602

NBS

U.S. DEPARTMENT OF COMMERCE

NATIONAL BUREAU OF STANDARDS

THE NATIONAL BUREAU OF STANDARDS

The National Bureau of Standards is a principal focal point in the Federal Government for assuring maximum application of the physical and engineering sciences to the advancement of technology in industry and commerce. Its responsibilities include development and maintenance of the national standards of measurement, and the provisions of means for making measurements consistent with those standards; determination of physical constants and properties of materials; development of methods for testing materials, mechanisms, and structures, and making such tests as may be necessary, particularly for government agencies; cooperation in the establishment of standard practices for incorporation in codes and specifications; advisory service to government agencies on scientific and technical problems; invention and development of devices to serve special needs of the Government; assistance to industry, business, and consumers in the development and acceptance of commercial standards and simplified trade practice recommendations; administration of programs in cooperation with United States business groups and standards organizations for the development of international standards of practice; and maintenance of a clearinghouse for the collection and dissemination of scientific, technical, and engineering information. The scope of the Bureau's activities is suggested in the following listing of its four Institutes and their organizational units.

Institute for Basic Standards. Applied Mathematics. Electricity. Metrology. Mechanics. Heat. Atomic Physics. Physical Chemistry. Laboratory Astrophysics.* Radiation Physics. Radio Standards Laboratory:* Radio Standards Physics; Radio Standards Engineering. Office of Standard Reference Data.

Institute for Materials Research. Analytical Chemistry. Polymers. Metallurgy. Inorganic Materials. Reactor Radiations. Cryogenics.* Materials Evaluation Laboratory. Office of Standard Reference Materials.

Institute for Applied Technology. Building Research. Information Technology. Performance Test Development. Electronic Instrumentation. Textile and Apparel Technology Center. Technical Analysis. Office of Weights and Measures. Office of Engineering Standards. Office of Invention and Innovation. Office of Technical Resources. Clearinghouse for Federal Scientific and Technical Information.**

Central Radio Propagation Laboratory.* Ionospheric Telecommunications. Tropospheric Telecommunications. Space Environment Forecasting. Aeronomy.

---

* Located at Boulder, Colorado 80301.

** Located at 5285 Port Royal Road, Springfield, Virginia 22171.

NATIONAL BUREAU OF STANDARDS REPORT

NBS PROJECT		NBS REPORT
221-11-2210461	November 30, 1965	9008

AN ELECTRIC QUADRUPOLE TRANSITION IN THE $A\ {}^1\Pi \leftarrow X\ {}^1\Sigma^+$ SYSTEM OF CO

by

S. G. Tilford and J. D. Simmons

Technical Report
to
National Aeronautics and Space Administration
Washington, D. C.

NASA Order No. R-64

NBS

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

Preface

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

AN ELECTRIC QUADRUPOLE TRANSITION IN THE $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$ SYSTEM OF CO

by

S. G. Tilford* and J. D. Simmons**

N66-16698

Abstract

In the fourth positive system, $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$, of CO electric quadrupole transitions ($\Delta J = 2$) have been observed for the first time in bands of an electric dipole allowed transition. The quadrupole transition probability has been determined to be $\sim 1.1 \times 10^3$ sec^{-1}. This value compares well with the value of $\sim 2.0 \times 10^3$ sec^{-1} determined for the quadrupole transition probability of the electric dipole forbidden $a\ ^1\Pi_g \leftarrow X\ ^1\Sigma_g^+$ transition in the isoelectronic N_2 molecule.

author

---

* E. O. Hulburt Center for Space Research, U. S. Naval Research Laboratory, Washington, D. C. 20390.

Work supported in part by the Office of Naval Research and the National Science Foundation.

** Work supported in part by the National Aeronautics and Space Administration.

During the reinvestigation of the high-resolution absorption spectra of the forbidden transitions of carbon monoxide in the vacuum ultraviolet $^{1)}$ several weak lines were observed at the head of each of the strong fourth positive system, $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$, bands. These lines cannot be identified with any of the known systems of CO which occur in this region; $a\ ^3\Pi \leftarrow X\ ^1\Sigma^+$, $a'\ ^3\Sigma^+ \leftarrow X\ ^1\Sigma^+$, $e\ ^3\Sigma^- \leftarrow X\ ^1\Sigma^+$, $d\ ^3\Delta \leftarrow X\ ^1\Sigma^+$, or $I\ ^1\Sigma^- \leftarrow X\ ^1\Sigma^+$. Similarily, the extra lines cannot be correlated with any isotopic analogues of the fourth positive system since appreciable quantities of stable species lighter than C^{12} and O^{16} do not exist.

A possible explanation of these lines is that they should be associated with bands of the fourth positive system. For this to be true, the selection rule $\Delta J = +2$ would have to be imposed. That such is the case is illustrated in Table I in which lines of the S(J) branch ($\Delta J = +2$) calculated from the observed P(J) and R(J) branches (which terminate on the Π_+ levels of the $A\ ^1\Pi$ state) are compared with observed transitions. The observed (P(J) and R(J) branches, rather than the rotational constants, were used to calculate the S(J) branch since there is an indication of a weak perturbation at low J values in the $v' = 4$ level of the $A\ ^1\Pi$ state as a result of interaction with the $v = 14$ level of the $a'\ ^3\Sigma^+$ state$^{2)}$.

The $A\ {}^1\Pi \leftarrow X\ {}^1\Sigma^+$ transition in CO is an electric dipole transition. Since $\Delta J = 2$ transitions are rigorously forbidden for electric dipole radiation[3], the observed lines must be attributed to electric quadrupole radiation. This is, therefore, the first example in which electric quadrupole lines have been observed for an electric dipole allowed transition.

The selection rules for electric quadrupole radiation are $+ \leftrightarrow +$, $- \leftrightarrow -$, and $+ \not\leftrightarrow -$, just the opposite of those for electric dipole radiation, thus, the S(J) branch terminates on the Π_+ levels as do the P(J) and R(J) branches. An O(J) branch ($\Delta J = -2$) should also be observed. However, because of the strength of the electric dipole (P(J), Q(J), and R(J) branches and also branches of the isotopic $C^{13}O^{16}$ and $C^{12}O^{18}$ molecules which occur in the same region, we have not been able to assign any O(J) lines. From the relative orders of magnitude of transition probabilities for electric dipole to magnetic dipole to electric quadrupole radiation ($1 : 1.3 \times 10^{-5} : 4.1 \times 10^{-7}$ at 1418 Å taking into account the ν^2 term in the quadrupole contribution);[4] P(J), Q(J), and R(J) branches resulting from magnetic dipole transitions should also be observed in this region. The branches would be similar to those observed for the stronger electric dipole transition except the (P(J) and R(J) branches would terminate on the Π_- levels and the Q(J) branch would terminate on the Π_+ levels, just the opposite of those for electric dipole radiation. Since the Λ - type doubling is almost negligible for bands of the fourth positive system the magnetic dipole branches will be very difficult to observe except in regions where strong perturbations of only one Λ - type component of the Π state are found.

In Fig. 1 the (4 - 0) band of the $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$ transition is illustrated. These spectrograms were photographed in the 4th order of the 21-foot vacuum spectrograph at the Naval Research Laboratory. A microwave excited krypton lamp was used as a source of background continuum5). The lower spectrogram in Fig. 1 was obtained with a path length of approximately 4×10^{-2} meter-atmos. The upper photograph required only approximately 5×10^{-7} meter-atmos. The extra lines beyond the head of the (4 - 0) A - X band in the high pressure spectrum in Fig. 1 are high J transitions in the (7 - 0) band of the $e\ ^3\Sigma^- \leftarrow X\ ^1\Sigma^+$ system (this corresponds to the (6 - 0) band reported earlier2,6). The weaker lines in the lower pressure spectrum belong to the (14 - 0) band of the $a'\ ^3\Sigma^+ \leftarrow X\ ^1\Sigma^+$ system and the $C^{13}O^{16}$ (4 - 0) band of $A\ ^1\Pi \leftarrow X\ ^1\Sigma^+$.

The spectra were first observed with the CO gas admitted directly into the body of the spectrograph. However, upon measurement of the proposed S(J) lines, we found that the lines were shifted from the positions calculated by use of the selection rule $\Delta J = +2$, by amounts up to approximately 1 cm^{-1} toward longer wavelengths. This shift was caused by the variation of the refractive index of the gas as a function of wavelength.

Near an absorption band the refractive index may be written

$$n^2 \propto \left(1 + \sum_i \frac{\rho_i}{(\nu_i^2 - \nu^2) + \dfrac{g_i \nu^2}{(\nu_i^2 - \nu^2)}} \right) \qquad (1)$$

where ν_i corresponds to the band origin, ρ_i is a constant and g_i is related to the width of the absorption band or line.7) The summation takes into account all absorption bands. From equation (1) it can be seen that as the wavelength approaches that a strong absorption band, the refractive index can change by a large amount in a short wavelength region. When ν is greater than ν_i the refractive index becomes less than unity and the observed wavelength is greater than the corresponding vacuum wavelength (this is just the reverse for wavelengths normally observed in the visible and near ultraviolet regions) in agreement with our observations. Subsequent experiments with an absorption cell placed in front of the slit verified that we were observing a refractive shift very close to the band origin.

The appearance pressure necessary to observe the S(J) branch was approximately 9×10^4 greater than that necessary to observed the R(J) branch with an identical path length.

This value is not too discordant with the order of magnitude of 2.4×10^6 indicated above for the ratio of transition probabilities of an electric dipole to an electric quadrupole transition. From the absolute values of transition probabilities for the fourth positive system recently determined by phase-shift techniques8) a value of approximately 1.1×10^3 sec^{-1} can be inferred for the absolute quadrupole transition probability observed here. The corresponding lifetime for the quadrupole transition would be approximately 9×10^{-2} sec.

From a rotational intensity analysis, the ratio of 0.33 between the relative transition probabilities of electric quadrupole to magnetic dipole radiation has recently been determined for the electric dipole forbidden $a\ {}^1\Pi_g \leftarrow X\ {}^1\Sigma_g^+$ transition in the iso-electronic N_2 molecule.9) From this value and the absolute transition probability of 5.9×10^3 sec^{-1} measured for the magnetic dipole $a\ {}^1\Pi_g \leftarrow X\ {}^1\Sigma_g^+$ transition in N_2 by a molecular beam technique,10) the absolute quadrupole transition probability in N_2 is calculated to be $\sim 2.0 \times 10^3$ sec^{-1}.

The quadrupole transition probability for the a - X transition in N_2 is approximately 1.8 times greater than that for the A - X transition in CO. This is in good agreement with the observation that to observe the CO quadrupole lines it is necessary to employ approximately 2.5 times the path length that is required to observe the N_2 quadrupole lines.

It should be pointed out that in both N_2 and CO no consideration has been taken into account for any possible line width variation for branches resulting from the different types of radiations. In the case of the quadrupole rotation-vibration spectrum of H_2, extremely small line widths have been observed, even at very high pressures[11, 12]).

The only other example of an electric quadrupole transition which has been reported is the $b\ {}^1\Sigma_g^+ - a\ {}^1\Delta_g$ transition in molecular oxygen at 1.9 microns in the infrared[13]). The reported transition moment of 2.5×10^{-3} sec^{-1} would correspond to 4.5×10^{-1} sec^{-1} had this transition been observed at 1400 Å. The $B\ {}^3\Pi_g \leftarrow X\ {}^1\Sigma_g^+$ transition in N_2 has also been observed, but no pure quadrupole lines in this system have yet been detected [14]).

The ratio of intensity contributions from electric quadrupole to electric dipole radiation is given by [3, 15, 16])

$$\frac{I_q}{I_d} = \frac{3\Pi^2\nu^2}{10} \cdot \frac{S_q}{S_d} \cdot X^2 \qquad (2)$$

where ν is the frequency, S_q and S_d are the appropriate line strength factors for an electric quadrupole and electric dipole transition, respectively, and X^2 is the ratio between quadrupole matrix elements and dipole matrix elements.

Upon substitution of the observed appearance pressures which are inversely proportional to the intensities, the appropriate line strength factors for the R(J) branch[3]) and the S(J) branch[16]) and a value of 70500 cm^{-1} for the frequency, a value of 2.5×10^{-16} is obtained for the observed ratio of quadrupole to dipole matrix elements. A crude theoretical prediction give an order of magnitude of 3.6×10^{-16} for the ratio of quadrupole to dipole matrix elements[4].

ACKNOWLEDGEMENT

The authors wish to express their appreciation to Mr. Vincent Franklin and Mr. Rudolph Naber for setting up the equipment and obtaining much of the experimental data.

REFERENCES

1. J. D. Simmons, A. M. Bass, G. Herzberg, T. J. Hugo, and S. G. Tilford (to be published).
2. J. D. Simmons, A. M. Bass, and S. G. Tilford (to be published).
3. G. Herzberg "Spectra of Diatomic Molecules" D. Van Nostrand and Co., Inc. Princeton, New Jersey (1950) pp.277, 127.
4. H. Eyring, J. Walter, and G. E. Kimball "Quantum Chemistry" John Wiley and Sons Inc., New York, N.Y. (1944) p. 115.
5. P. G. Wilkinson and E. T. Byram, Applied Optics, 4, 581 (1965).
6. G. Herzberg and T. J. Hugo, Can. J. Physics, 33, 757 (1955).
7. R. W. Wood, "Physical Optics" The Macmillan Co. New York, N. Y. (1934) p. 489.
8. J. E. Hesser and K. Dressler, Astrophys. J., 142, 389 (1965).
9. J. T. Vanderslice, P. G. Wilkinson, and S. G. Tilford, J. Chem. Phys., 42, 2681 (1965).
10. W. Lichten, J Chem. Phys., 26, 306 (1957).
11. G. Herzberg, Can. J. Research, 28A, 144 (1950).
12. D. H. Rank and T. A. Wiggins, J. Chem. Phys., 39, 1110 (1963).
13. J. F. Noxon, Can. J. Phys., 39, 1110 (1961).
14. P. G. Wilkinson, J. Quant, Spect. Radiat. Trans., 2, 343 (1962).
15. E. O Condon and G. H Shortley "Theory of Atomic Spectra" Cambridge University Press. New York, N.Y. (1951) pp 91-96.
16. Y. N. Chiu, J. Chem. Phys., 42, 2671 (1965).

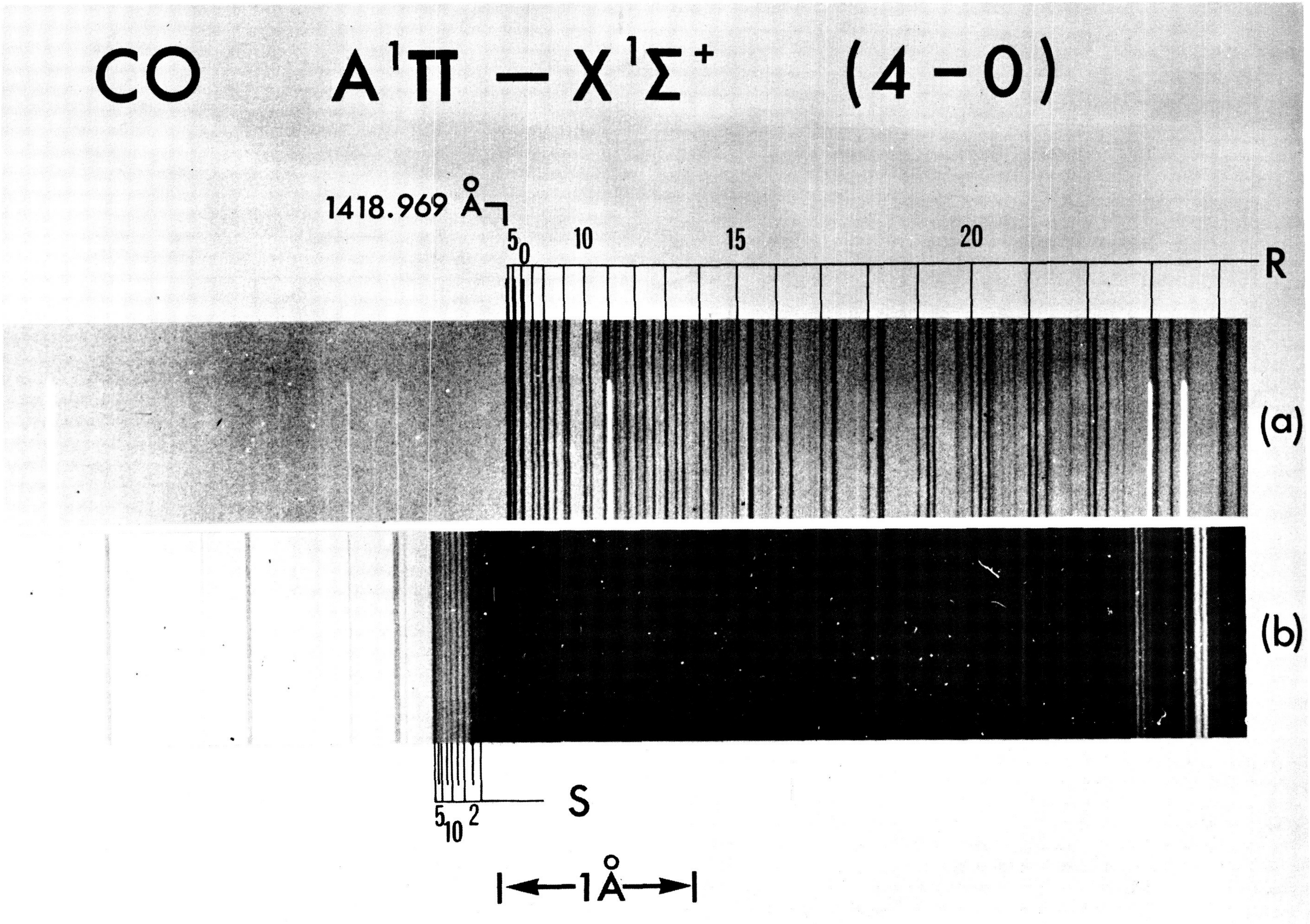
CAPTIONS TO FIGURES

Fig. 1 The (4 - 0) absorption band of the A $^1\Pi \leftarrow X\ ^1\Sigma^+$ transition in CO. (a) Low pressure spectrogram with the R(J) electric dipole branch illustrated. (b) High pressure spectrogram with the S(J) electric quadrupole branch illustrated.

TABLE 1

	S(J) cm^{-1}	
J	calculated	observed
1	70481.00	70480.80*
2	485.28	485.24
3	488.77	488.78
4	491.37	491.52
5	493.30	493.41
6	494.31	494.26*
7	494.79	494.37*
8	494.01	493.87*
9	492.58	492.66
10	490.44	490.36
11	487.24	487.25
12	483.48	483.40

* blended


CO $A^1\Pi - X^1\Sigma^+$ (4-0)
1418.969 Å
5
0
10
15
20
R
(a)
(b)
S
5
10
2
1Å