Infrared Absorption Spectroscopy of the CO–Ar Complex

A. R. W. McKellar

*Herzberg Institute of Astrophysics, National Research Council of Canada,
Ottawa, Ontario K1A 0R6, Canada*

AND

Y. P. Zeng, S. W. Sharpe,[1] C. Wittig, and R. A. Beaudet

Department of Chemistry, University of Southern California, Los Angeles, California 90089-0482

The rotation–vibration spectrum of the weakly bound complex CO–Ar has been studied in the 2140 cm^{-1} region of the fundamental band of CO. Data were obtained from two different experiments: first, a pulsed slit-jet supersonic expansion and a tunable diode laser source; and second a long-path low-temperature static gas cell and a Fourier transform spectrometer. The low rotational temperature and narrow line width of the jet expansion data were complementary to the higher J-values and broad coverage of the static cell data. The observed spectrum was approximately that of a T-shaped near-prolate asymmetric rotor molecule. About 370 transitions were assigned to 6 perpendicular subbands with K = 3–2, 2–1, 1–0, 0–1, 1–2, and 2–3. No parallel ($\Delta K = 0$) subbands were observed. The observed B rotational constant of the complex in its ground state, 0.0691 cm^{-1}, corresponds to an effective intermolecular separation of about 3.850 Å. The observed A rotational constant of about 2.47 cm^{-1} is not too far from the $\bar{B}$ value of the CO monomer, 1.92 cm^{-1}, as expected for the approximately T-shaped effective geometry of the complex.
© 1992 Academic Press, Inc.

I. INTRODUCTION

In recent years, tremendous progress has been made in the study of weakly bound molecular complexes by employing spectroscopic techniques in the microwave, infrared, and visible wavelength regions. Such spectra provide the most precise means to probe intermolecular forces in the attractive region, and the results are of key importance for understanding molecular energy transfer and collisional dynamics. The van der Waals complex CO–Ar is one of the simplest of weakly bound species, but until now no analysis of its spectrum has appeared. The only published account of CO–Ar was made by De Piante *et al.* (*1*), who included portions of its infrared spectrum in a paper dealing mostly with experimental technique.

In the present paper, we report extensive measurements and analysis of this same infrared spectrum of CO–Ar, which occurs in the 4.7-μm region of the fundamental band of CO. Our study combines the results of two rather different experimental techniques. The first involves the use of a pulsed slit-jet supersonic expansion together with a rapid-scan tunable diode laser spectrometer; this is similar to the apparatus employed by De Piante *et al.* (*1*). The second involves a long-path low-temperature

---

[1] Present address: Battelle Pacific Northwest Laboratory, Battelle Blvd., P.O. Box 999, Richland, WA 99352.

absorption cell containing an equilibrium CO + Ar mixture together with a Fourier transform spectrometer (FTS). The supersonic jet/laser spectra have the advantage of very low ($\simeq$10 K) rotational temperature, narrow linewidth (and hence accurate line position measurement), and freedom from interference by CO monomer absorption lines. In contrast, the long-path FTS spectra suffer from greater linewidth and interference from monomer absorption. However, their higher temperature ($\simeq$60 K) and wide coverage are complementary to the jet/laser spectra, and help to extend the analysis to higher J-values.

The only detailed theoretical calculations on the bound energy levels of CO–Ar to have been published are those of J. Tennyson and co-workers (2), who used the potential energy surface of Mirsky (3). In their work, both classical and exact quantum calculations were performed using a realistic empirical potential surface, and attention was directed at the onset of irregular behavior in the structure of the rovibrational energy levels. The results are useful for understanding the general pattern of the CO–Ar levels, but they were not complete enough to be directly applied in analyzing our observed spectra.

II. EXPERIMENTAL DETAILS

The supersonic jet measurements were made in Los Angeles using the apparatus described in previous publications (4–7). Briefly, tunable infrared radiation from a tunable diode laser was directed into the vacuum chamber and multipassed through the jet from a pulsed supersonic slit source with dimensions 38 × 0.15 mm. A small portion of the infrared beam was diverted through a reference gas cell and an etalon for wavenumber calibration. Spectra were measured by rapidly scanning (0.5 cm^{-1} msec^{-1}) the diode laser, and simultaneously recording the jet, reference, and etalon signals using fast InSb detectors and CAMAC based digitizers. The repetition rate for the jet was 3 Hz, and a typical spectrum covering 0.5 cm^{-1} required the average of 100 pulses and took about one-half minute to acquire. Typical conditions for forming CO–Ar were 10–20% CO in argon with backing pressures of 1 atm for the free expansion into vacuum.

The long-path FTS measurements were made in Ottawa using the same apparatus used in recent studies of hydrogen dimers (8) and CO–H$_2$/D$_2$ complexes (9). Spectra were recorded with a Bomem Model DA3.002 spectrometer fitted with a CaF$_2$ beamsplitter and InSb detector. The 3.5-m absorption cell was set for 24 traversals to give a total path of 84 m. It was cooled using a Philips PGH-105 cryogenerator to a temperature ($\simeq$60 K) close to the lowest consistent with the chosen partial pressures of CO and Ar (about 0.3 and 5 Torr, respectively). In the spectrum used for the measurements reported here, the spectral resolution was 0.007 cm^{-1} (apodized), and the data accumulation time was 13 hr. Tests using pure CO confirmed that no significant absorptions due to CO dimers were present in the spectra. Portions of these FT spectra of CO–Ar have been shown previously in Fig. 3 of Ref. (9) and in Fig. 8 of Ref. (10).

III. ANALYSIS

It is shown by theory (2), and is qualitatively evident from our spectra, that CO–Ar behaves approximately as a T-shaped near-prolate asymmetric rotor molecule, with K_a as a good quantum number. However, CO–Ar is also a very nonrigid species, with large amplitude bending and intermolecular stretching modes, and we thus chose not to use an asymmetric rotor Hamiltonian in this work. Instead we adopted a very

simple near symmetric rotor energy level expression, similar to those frequently used to analyze linear and nonlinear triatomic van der Waals molecules:

$$E_{\text{rot}} = \bar{B}[J(J+1) - K^2] - D[J(J+1) - K^2]^2 + H[J(J+1) - K^2]^3 + \Delta E_K, \quad (1)$$

$$\Delta E_K = \pm\{(\tfrac{1}{4})(B - C)J(J+1) + (\tfrac{1}{2})d[J(J+1)]^2 + (\tfrac{1}{2})h[J(J+1)]^3\}.$$

In this expression, the asymmetry splitting term, ΔE_K, is zero for $K = 0$; all three parameters in ΔE_K are allowed for $K = 1$; only d and h are allowed for $K = 2$; and only h is allowed for $K = 3$. The origins of each stack of levels denoted by $K = 0, 1, 2,$ or 3 (and by $v_{\text{CO}} = 0$ or 1) were additional parameters in the analysis.

The precision of the supersonic jet data used in the analysis was about 0.0003 cm^{-1}. The precision of the FTS data, which was somewhat dependent on individual linestrengths and on possible blends, was about 0.0010 cm^{-1} or better. In a sample of 58 transitions belonging to the $K = 1$–0 and 0–1 subbands for which the two data sources overlapped, their agreement was excellent, with an rms deviation between the two sources of only 0.00055 cm^{-1}. In the least-squares analysis of the spectrum reported below, the FTS data were given a relative weight of 0.2 to reflect their lower precision.

A. The K = 1–0 and 0–1 Subbands

The CO–Ar spectrum in the central region near the CO band origin is dominated by the prominent $K = 1$–0 and 0–1 subbands, and these were a natural place to start the analysis. Measured line positions and assignments are shown for these two subbands in Tables I and II, respectively. For much of these subbands, the laser and FTS data sources overlapped, but since the precision of the laser data was superior, we used these values when available. However, the cold jet/laser data only extended to $J = 16$ to 23, depending on the branch, and thus the hotter FTS data were used to extend the analysis up to J-values of 25 to 30. Note that the P and R branches in Tables I and II involve transitions beginning or ending on the lower component of the $K = 1$ asymmetry doublet (lower sign choice in Eq. (1)), whereas the Q branches involve the upper component (upper sign choice).

In the $K = 1$–0 subband, $Q(1)$ through $Q(20)$ were available from the laser data, and this could be extended up to $Q(28)$ using the FTS data. Assignments for $Q(29)$ and $Q(30)$ are also listed in Table I, but their positions rapidly diverged from the calculated values (even if higher order parameters were fitted) and they were given zero weight in the fit. Information on the $K = 1$–0 R branch came entirely from the laser data. However the R branch was calculated to form a head at a position of 2147.506 cm^{-1} corresponding to $R(27)$. In the FT spectrum this head was indeed observed, though at a slightly lower frequency of 2147.495 cm^{-1}. The P branch of $K = 1$–0 was measured in the laser spectrum from $P(2)$ to $P(18)$ and then extended by the FT spectrum from $P(19)$ to $P(27)$. The next lines, $P(28)$ and $P(29)$, were obscured by the strong Q branch of the $K = 0$–1 subband. $P(30)$ was weakly observed at a slightly perturbed position, but not included in the fit (see Table I).

Turning to the $K = 0$–1 subband in Table II, the Q branch was observed from $J = 1$ to 23 in the laser spectrum, and $Q(24)$ to $Q(30)$ were added from the FT spectrum. However, above $Q(27)$ the line positions deviated from the calculated values, and the measurements were given zero weight in the fit. The situation was similar to that arising in the $K = 1$–0 Q branch, except that the apparent perturbation affecting the lines occurred about one J-value lower here. Note that the sign of the deviations is

TABLE I

Transitions in the $K = 1$–0 Subband of CO–Ar (in cm^{-1})[a]

J	P(J) Observed	O-C	R(J) Observed	O-C	Q(J) Observed	O-C
0			2145.2924 L	0.0003		
1			2145.4251 L	0.0005	2145.1588 L	0.0005
2	2144.8776 L	0.0000	2145.5542 L	0.0001	2145.1617 L	0.0003
3	2144.7336 L	-0.0003	2145.6807 L	0.0001	2145.1662 L	0.0001
4	2144.5875 L	-0.0001	2145.8042 L	0.0000	2145.1723 L	0.0000
5	2144.4387 L	0.0002	2145.9245 L	-0.0001	2145.1800 L	0.0001
6	2144.2868 L	0.0000	2146.0417 L	-0.0001	2145.1891 L	-0.0001
7	2144.1320 L	-0.0005	2146.1556 L	-0.0002	2145.1999 L	0.0000
8	2143.9756 L	-0.0002	2146.2667 L	-0.0003	2145.2119 L	-0.0003
9	2143.8166 L	0.0001	2146.3734 L	-0.0002	2145.2259 L	-0.0002
10	2143.6545 L	-0.0002	2146.4776 L	0.0002	2145.2410 L	-0.0004
11	2143.4903 L	-0.0002	2146.5772 L	-0.0003	2145.2578 L	-0.0004
12	2143.3241 L	0.0003	2146.6735 L	-0.0004	2145.2765 L	-0.0001
13	2143.1552 L	0.0003	2146.7659 L	-0.0004	2145.2963 L	-0.0001
14	2142.9833 L	-0.0001	2146.8544 L	-0.0003	2145.3178 L	-0.0001
15	2142.8096 L	0.0000	2146.9387 L	-0.0001	2145.3410 L	0.0002
16	2142.6337 L	0.0003	2147.0189 L	0.0005	2145.3655 L	0.0002
17	2142.4545 L	-0.0002	2147.0931 L	-0.0002	2145.3918 L	0.0005
18	2142.2736 L	0.0000	2147.1629 L	-0.0003	2145.4195 L	0.0006
19	2142.0903 F	0.0003	2147.2281 L	0.0002	2145.4486 L	0.0006
20	2141.9034 F	-0.0004	2147.2873 L	0.0004	2145.4791 L	0.0003
21	2141.7155 F	0.0006	2147.3402 L	0.0002	2145.5114 F	0.0002
22	2141.5229 F	-0.0004	2147.3869 L	0.0003	2145.5441 F	-0.0012
23	2141.3286 F	-0.0002	2147.4259 L	-0.0005	2145.5796 F	-0.0015
24	2141.1303 F	-0.0009	(2147.4588)		2145.6173 F	-0.0013
25	2140.9291 F	-0.0013	(2147.4833)		2145.6562 F	-0.0018
26	2140.7270 F	0.0010	(2147.4993)		2145.6978 F	-0.0015
27	2140.5185 F	0.0005	(2147.5060)[b]		2145.7419 F	-0.0007
28	(2140.3058)		(2147.5027)		2145.7909 F	0.0029
29	(2140.0893)		(2147.4886)		2145.8499 f	0.0144
30	2139.8491 f	-0.0189	(2147.4629)		2145.9241 f	0.0387

[a]Values in parentheses are calculated line positions.
 L = Laser observation, given a weight of 1.0 in the fit.
 F = FTS observation, given a weight of 0.2 in the fit.
 f = FTS observation, given a weight of zero in the fit.
[b]This unresolved R-branch head was observed in the FT spectrum at 2147.495 cm^{-1}.

opposite (negative here, positive in Table I) for the two Q branches, just as expected if they arise from analogous causes. The P branch was observed from $P(1)$ to $P(16)$ in the laser data, and this was extended up to $P(25)$ using the FT data. Above $P(25)$ the branch turns around, forming a bandhead, and the lines were too closely spaced to be reliably determined from the FT spectrum. This P-branch head, which was calculated to occur at $P(28)$ and 2138.150 cm^{-1}, was actually observed in the FT spectrum at about 2138.170 cm^{-1}. Again, the situation was just the mirror image of the $K = 1$–0 subband with its R-branch head at 2147.5 cm^{-1}. The R branch for $K = 0$–1 was measured in the laser spectrum from $R(1)$ to $R(18)$ and extended up to $R(26)$ using the FT spectrum. Beyond this point, the lines were obscured in the FT spectrum by the strong $K = 1$–0 Q branch.

TABLE II

Transitions in the $K = 0–1$ Subband of CO-Ar (in cm^{-1})[a]

J	P(J)		R(J)		Q(J)	
	Observed	O–C	Observed	O–C	Observed	O–C
1	2140.3485 1	-0.0015	2140.7655 L	0.0010	2140.4831 L	-0.0007
2	2140.2173 L	-0.0001	2140.9091 L	0.0008	2140.4804 L	-0.0005
3	2140.0878 L	0.0000	2141.0553 L	0.0007	2140.4759 L	-0.0004
4	2139.9611 L	-0.0001	2141.2042 L	0.0005	2140.4698 L	-0.0004
5	2139.8373 L	-0.0003	2141.3556 L	0.0004	2140.4624 L	-0.0003
6	2139.7172 L	0.0000	2141.5093 L	-0.0001	2140.4535 L	-0.0002
7	2139.5998 L	0.0000	2141.6660 L	-0.0002	2140.4429 L	-0.0002
8	2139.4856 L	-0.0002	2141.8252 L	-0.0002	2140.4308 L	-0.0003
9	2139.3751 L	0.0000	2141.9863 L	-0.0009	2140.4173 L	-0.0002
10	2139.2681 L	0.0003	2142.1522 F	0.0009	2140.4023 L	-0.0002
11	2139.1647 L	0.0006	2142.3181 L	0.0002	2140.3857 L	-0.0002
12	2139.0646 L	0.0006	2142.4872 L	0.0003	2140.3678 L	-0.0001
13	2138.9681 L	0.0003	2142.6588 L	0.0004	2140.3485 L	0.0000
14	2138.8759 L	0.0004	2142.8323 L	0.0000	2140.3274 L	-0.0001
15	2138.7875 L	0.0002	2143.0085 L	-0.0002	2140.3048 L	-0.0002
16	2138.7038 L	0.0002	2143.1879 L	0.0002	2140.2811 L	-0.0001
17	2138.6245 F	0.0002	2143.3692 L	0.0000	2140.2557 L	-0.0003
18	2138.5489 F	-0.0010	2143.5530 L	-0.0002	2140.2290 L	-0.0001
19	2138.4797 F	-0.0008	2143.7408 F	0.0007	2140.2008 L	-0.0002
20	2138.4159 F	-0.0007	2143.9299 F	0.0001	2140.1713 L	-0.0001
21	2138.3568 F	-0.0016	2144.1227 F	0.0003	2140.1404 L	0.0000
22	2138.3069 F	0.0006	2144.3181 F	-0.0001	2140.1083 L	0.0003
23	2138.2604 F	-0.0003	2144.5175 F	0.0002	2140.0746 L	0.0002
24	2138.2215 F	-0.0007	2144.7204 F	0.0004	2140.0393 F	0.0000
25	2138.1927 F	0.0015	2144.9276 F	0.0012	2140.0034 F	0.0005
26	(2138.1684)		2145.1356 F	-0.0014	2139.9641 F	-0.0011
27	(2138.1543)		(2145.3520)		2139.9231 f	-0.0031
28	(2138.1497)[b]		(2145.5718)		2139.8789 f	-0.0070
29	(2138.1552)		(2145.6990)		2139.8266 f	-0.0178
30	(2138.1718)		(2146.8087)		2139.7586 f	-0.0431

[a]Values in parentheses are calculated line positions.
L = Laser observation, given a weight of 1.0 in the fit.
1 = Laser observation, given a weight of zero in the fit due to
   blending with Q(13).
F = FTS observation, given a weight of 0.2 in the fit.
f = FTS observation, given a weight of zero in the fit.
[b]This unresolved P-branch head was observed in the FT spectrum
   at 2138.169 cm^{-1}.

B. The $K = 2–1$ and $1–2$ Subbands

The next strongest features in the observed spectra were the $K = 2–1$ and $1–2$
subbands. Their origins were marked by unresolved Q branches in the FT spectrum
at about 2149.3 and 2136.25 cm^{-1}, respectively. The assignments of individual lines
in these subbands could be made relatively easily and unambiguously thanks to the
fact that the $K = 1$ energy levels were already very well determined from preliminary
fits to the $K = 1–0$ and $0–1$ subbands.

For the $K = 2–1$ subband, the Q branches were observed in the laser spectrum from
$Q(3)$ to $Q(17)$ for one asymmetry-doubled component, and from $Q(2)$ to $Q(14)$ for
the other. The R branches were observed from $R(1)$ to $R(18)$ for both components,

TABLE III

Transitions in the $K = 2-1$ Subband of CO–Ar (in cm^{-1})^a

J	P$_1$(J) Calculated	P$_2$(J) Calculated	R$_1$(J) Observed	O–C	R$_2$(J) Observed	O–C	Q$_1$(J) Observed	O–C	Q$_2$(J) Observed	O–C
1			2149.5400 L	−0.0001	2149.5358 L	0.0001				
2			2149.6767 L	0.0000	2149.6638 L	−0.0001	(2149.2694)		2149.2565 L	0.0002
3	2148.8634	2148.8374	2149.8136 L	−0.0001	2149.7880 L	0.0000	2149.2706 L	−0.0003	2149.2449 L	0.0000
4	2148.7298	2148.6865	2149.9511 L	0.0004	2149.9086 L	0.0004	2149.2725 L	−0.0004	2149.2293 L	0.0000
5	2148.5967	2148.5320	2150.0881 L	0.0004	2150.0242 L	0.0001	2149.2753 L	−0.0002	2149.2099 L	0.0001
6	2148.4643	2148.3739	2150.2245 L	0.0001	2150.1360 L	0.0001	2149.2783 L	−0.0002	2149.1863 L	0.0002
7	2148.3323	2148.2122	2150.3603 L	−0.0002	2150.2433 L	−0.0001	2149.2819 L	−0.0001	2149.1581 L	0.0000
8	2148.2007	2148.0469	2150.4958 L	0.0000	2150.3467 L	0.0002	2149.2856 L	0.0000	2149.1256 L	0.0002
9	2148.0695	2147.8781	2150.6294 L	−0.0005	2150.4454 L	0.0003	2149.2901 L	−0.0003	2149.0881 L	0.0001
10	2147.9382	2147.7058	2150.7619 L	−0.0004	2150.5393 L	0.0002	2149.2962 L	−0.0001	2149.0453 L	0.0001
11	2147.8069	2147.5300	2150.8919 L	−0.0007	2150.6294 L	0.0011	2149.3008 L	0.0002	2148.9968 L	−0.0001
12	2147.6751	2147.3507	2151.0192 L	−0.0007	2150.7129 L	0.0002	2149.3066 L	0.0002	2148.9425 L	−0.0001
13	2147.5424	2147.1679	2151.1438 L	0.0001	2150.7922 L	0.0000	2149.3126 L	0.0001	2148.8814 L	0.0000
14	2147.4085	2146.9816	2151.2630 L	−0.0002	(2150.8663)		2149.3192 L	0.0001	2148.8131 L	0.0002
15	2147.2727	2146.7919	2151.3777 L	0.0005	2150.9351 L	−0.0001	2149.3263 L	0.0001	2148.7345 F	−0.0014
16	2147.1344	2146.5987	2151.4849 L	0.0003	2150.9984 L	−0.0001	2149.3332 L	−0.0005	2148.6509aF	0.0013
17			2151.5842 L	0.0001	2151.0560 L	−0.0001	2149.3415 L	−0.0001	2148.5565aF	0.0037
18			2151.6740 L	−0.0003	2151.1074 L	−0.0004	(2149.3501)		2148.4437 F	−0.0004
19			2151.7526 F	−0.0006	2151.1557 F	0.0024	(2149.3592)		2148.3221 F	0.0002
20			(2151.8190)		2151.1922 F	0.0000	(2149.3688)		(2148.1845)	
21			(2151.8694)		2151.2284 f	0.0039				

^{a} Values in parentheses are calculated line positions.
  L = Laser observation, given a weight of 1.0 in the fit.
  F = FTS observation, given a weight of 0.2 in the fit (aF = weight of 0.1, due to blending).
  f = FTS observation, given a weight of zero in the fit.

but no lines were observed for the weaker P branches. The data are listed in Table III. It was only possible to extend the analysis a small amount using the FT spectrum. The problem was not so much that the lines were weak, but rather that the density of other interfering lines was much higher here in the FT spectrum than in the $K = 1$–

TABLE IV

Transitions in the $K = 1-2$ Subband of CO–Ar (in cm^{-1})^a

J	P$_1$(J) Observed	O–C	P$_2$(J) Observed	O–C	R$_1$(J) Calculated	R$_2$(J) Calculated	Q$_1$(J) Observed	O–C	Q$_2$(J) Observed	O–C
2	2136.0145 L	0.0000	2136.0185 L	−0.0004	2136.6909	2136.7172	2136.2848 L	−0.0003	2136.2987 L	0.0005
3	2135.8777 L	−0.0001	2135.8907 L	−0.0001	2136.8245	2136.8682	2136.2832 L	−0.0004	2136.3103 L	0.0004
4	2135.7409 L	0.0000	2135.7667 L	−0.0002	2136.9575	2137.0229	(2136.2815)		2136.3259 L	0.0004
5	2135.6038 L	−0.0001	2135.6468 L	−0.0002	2137.0899	2137.1813	2136.2796 L	0.0006	2136.3455 L	0.0002
6	(2135.4669)		2135.5310 L	−0.0003	2137.2218	2137.3433	2136.2764 L	0.0004	2136.3693 L	0.0001
7	(2135.3301)		(2135.4198)		2137.3533	2137.5089	2136.2729 L	0.0005	2136.3971 L	−0.0004
8	(2135.1938)		(2135.3126)		2137.4845	2137.6780	2136.2690 L	0.0005	2136.4300 L	−0.0002
9	(2135.0583)		(2135.2098)		2137.6155	2137.8506	2136.2645 L	0.0005	2136.4672 L	−0.0007
10	2134.9215 F	−0.0025	(2135.1114)		2137.7467	2138.0268	2136.2591 L	0.0000	2136.5100 L	−0.0006
11	2134.7926 F	0.0014	(2135.0176)		2137.8782	2138.2064	2136.2535 L	−0.0002	2136.5587 L	−0.0002
12	2134.6594 F	−0.0012	(2134.9286)		2138.0106	2138.3895	2136.2478 L	−0.0001	2136.6134 L	0.0000
13	(2134.5328)		2134.8448 F	0.0004	2138.1442	2138.5761	2136.2417 L	0.0000	2136.6746 L	0.0002
14	2134.4090 F	0.0013	(2134.7652)				2136.2349 L	−0.0001	2136.7434 L	0.0005
15	(2134.2886)		(2134.6912)				2136.2283 L	0.0003	(2136.8198)	
16	2134.1744 L	0.0002	2134.6225 F	−0.0002			2136.2206 L	0.0000	2136.9078 F	0.0016
17	2134.0679 F	0.0013	2134.5578 F	−0.0020			2136.2130 L	0.0005	2137.0037 F	0.0005
18	2133.9651 F	−0.0020	(2134.5029)				2136.2050 L	0.0001	2137.1128 F	0.0004
19	2133.8767 F	−0.0007	2134.4528 F	0.0006			2136.1965 L	0.0001	2137.2327 F	−0.0028
20	2133.7986 F	−0.0008	2134.4090 F	0.0009			(2136.1879)		2137.3764 F	0.0019
21	2133.7348 F	−0.0005	2134.3703 F	−0.0007			(2136.1791)		2137.5300 F	−0.0016
22	2133.6891 F	0.0016	(2134.3413)				(2136.1701)		2137.7099 F	0.0004
23	2133.6639 f	0.0052	(2134.3196)						2137.9151 f	0.0041

^{a} Values in parentheses are calculated line positions.
  L = Laser observation, given a weight of 1.0 in the fit.
  F = FTS observation, given a weight of 0.2 in the fit.
  f = FTS observation, given a weight of zero in the fit.

0 and 0–1 band regions. In any event, the assignments in Table III extend only to J-values of 17 to 21, as compared to $J \simeq 30$ in Tables I and II.

The situation for the $K = 1$–2 subband was similar to that of $K = 2$–1, except that it was possible to use more of the FTS data. The observed transitions are listed in Table IV. For the P branches, only a few low-J lines up to $P(6)$ were available from the laser spectrum, but fortunately it was possible to extend this up to $J = 21$ to 23 using the FT spectrum. No lines of the weak R branches were available from either source. The Q branches were well measured in the laser spectrum up to $Q(19)$ and $Q(14)$, and it was possible to extend one of these up to $Q(23)$ using the FT spectrum.

In Tables III and IV, the subscripts on each branch label, e.g., $P_1(J)$, $P_2(J)$, denote that the lower (1) or upper (2) sign choice (Eq. (1)) for the $K = 1$ asymmetry doublet is involved in the transition. For the P and R branches, each $K = 1$ level combines with the opposite component in $K = 2$ (that is, upper–lower, lower–upper), whereas for the Q branches, each combines with the same component in $K = 2$ (upper–upper, lower–lower). Here, upper and lower refer to the sign choice in Eq. (1) and not necessarily to the energy ordering of the levels. As pointed out below, the $K = 2$ levels are actually inverted in CO–Ar.

C. The K = 3–2 and 2–3 Subbands

The observed transitions and assignments for these subbands are given in Tables V and VI, respectively. The data were much less extensive than for the lower K-subbands, but fortunately the analysis was helped by the fact that the $K = 2$ energy levels were well determined from preliminary fits to the $K = 2$–1 and 1–2 subbands. Thus there were relatively few free parameters in the analysis. For the $K = 3$–2 subband (Table V), a good range of lines from $J = 2$ to 12 was measured for the R and Q branches in the laser spectrum, but no lines were observed in the P branches. For the $K = 2$–3 subband (Table VI), only a handful of lines in the P branches were available from the laser spectrum, and none were observed for the Q or R branches.

The difficulty in extending the analysis using FTS results was again due to the very high density of observed lines in the regions of interest. These lines must arise from other excited states of CO–Ar, for example the excited bending states. It should be noted that the FT spectrum was always consistent with the laser results, even when

TABLE V

Transitions in the $K = 3$–2 Subband of CO-Ar (in cm^{-1})[a]

J	$P_1(J)$ Calculated	$P_2(J)$ Calculated	$R_1(J)$ Observed	O–C	$R_2(J)$ Observed	O–C	$Q_1(J)$ Observed	O–C	$Q_2(J)$ Observed	O–C
2			2153.5460 L	0.0003	2153.5460 L	0.0003				
3			2153.6716 L	0.0005	2153.6716 L	0.0004				
4	2152.5962	2152.5959	2153.7939 L	0.0003	2153.7939 L	0.0001	2153.1286 L	-0.0004	2153.1286 L	-0.0001
5	2152.4511	2152.4505	2153.9132 L	0.0002	2153.9132 L	-0.0002	2153.1161 L	-0.0005	2153.1161 L	0.0003
6	2152.3037	2152.3025	2154.0292 L	0.0004	2154.0292 L	-0.0003	2153.1005 L	-0.0009	2153.1005 L	0.0006
7	2152.1541	2152.1520	2154.1414 L	0.0005	2154.1414 L	-0.0006	2153.0835 L	-0.0001	2153.0808 L	0.0001
8	2152.0021	2151.9987	2154.2476 L	-0.0010	2154.2501 L	0.0001	2153.0627 L	-0.0002	2153.0577 L	0.0001
9	2151.8475	2151.8423	2154.3503 L	-0.0010	2154.3535 L	0.0003	2153.0391 L	0.0000	2153.0311 L	0.0010
10	2151.6901	2151.6825	2154.4474 L	-0.0008	2154.4507 L	0.0003	2153.0121 L	0.0002	2152.9975 L	0.0002
11			2154.5384 L	0.0000	2154.5406 L	0.0001	2152.9820 L	0.0010	2152.9580 L	0.0000
12			2154.6207 L	0.0002	2154.6221 L	-0.0001	2152.9483 l	0.0024	2152.9104 L	-0.0004
13			2154.6987 l	0.0054	2154.6987 l	0.0053	(2153.9061)		(2152.8538)	

[a] Values in parentheses are calculated line positions.
  L = Laser observation, given a weight of 1.0 in the fit.
  l = Laser observation, given a weight of zero in the fit.

TABLE VI

Transitions in the $K = 2$-3 Subband of CO–Ar (in cm^{-1})[a]

J	P$_1$(J)		P$_2$(J)		R$_1$(J)	R$_2$(J)	Q$_1$(J)		Q$_2$(J)
	Observed	O-C	Observed	O-C	Calculated	Calculated	Observed	O-C	Calculated
3	(2131.8426)		(2131.8426)		2132.7932	2132.7930	(2132.2501)		2132.2500
4	(2131.7173)		(2131.7173)		2132.9389	2132.9383	(2132.2605)		2132.2601
5	(2131.5950)		(2131.5948)		2133.0871	2133.0858	(2132.2736)		2132.2728
6	2131.4758 L	-0.0001	2131.4758 L	0.0004	2133.2379	2133.2356	(2132.2897)		2132.2881
7	2131.3601 L	-0.0002	2131.3601 L	0.0006	2133.3915	2133.3877	(2132.3092)		2132.3061
8	2131.2474 L	-0.0010	2131.2474 L	0.0002	2133.5480	2133.5423	(2132.3325)		2132.3270
9	2131.1411 L	0.0001	2131.1389 L	-0.0003	2133.7079	2133.6997	(2132.3602)		2132.3508
10	2131.0387 L	0.0002	2131.0358 L	-0.0002	2133.8717	2133.8602	(2132.3932)		2132.3779
11	2130.9418 L	0.0001	2130.9388 L	0.0000			(2132.4325)		2132.4086
12	2130.8510 L	-0.0006	2130.8491 L	0.0007			2132.4792 f	-0.0006	2132.4435
13	2130.7673 l	-0.0021	2130.7673 l	0.0007			2132.5410 f	0.0043	2132.4829
14	(2130.6967)		(2130.6950)				2132.6163 f	0.0106	2132.5279
15							2132.7092 f	0.0196	2132.5792

[a] Values in parentheses are calculated line positions.
L = Laser observation, given a weight of 1.0 in the fit.
l = Laser observation, given a weight of zero in the fit.
f = FTS observation, given a weight of zero in the fit.

no FT data could be added to the analysis. For example, the (mostly unresolved) Q branches for $K = 3$-2 were quite evident in the FT spectrum at 2153.0 to 2153.15 cm^{-1}.

In Tables V and VI, the subscripts on each branch label denote the lower (1) or upper (2) sign choice (Eq. (1)) for the $K = 2$ component involved in the transition. For the P and R branches, each $K = 2$ level combines with the opposite component in $K = 3$ (that is, upper–lower, lower–upper), whereas for the Q branches, each combines with the same component in $K = 3$ (upper–upper, lower–lower).

D. The Molecular Parameters

The parameters resulting from a least-squares fit to the combined data of Tables I–VI are summarized in Table VII. They consist of six subband origins, as well as the rotational parameters for eight individual substates of CO–Ar, namely those with $K = 0$, 1, 2, and 3 for each of $v_{CO} = 0$ and 1. Simultaneous fitting of all the observed subbands ensured that, for example, the $v_{CO} = 1$, $K = 1$ parameters were determined not only from the $K = 1$-0 subband, but also from the $K = 1$-2 subband. In general, all the available parameters in Eq. (1) were adjusted for each of the six observed (v_{CO}, K) states, in addition to the six band origins. However, the limited data available from the $K = 2$-3 subband meant that only its origin and B-value for (v_{CO}, K) = 0, 3 could be varied in the fit, while the centrifugal distortion parameters D, H, and h were fixed at the values determined for the (v_{CO}, K) = 1, 3 state.

During the final stages of the fit, we noted the presence of small systematic residuals in the $K = 3$-2 subband. A comparison of the combination differences for (v_{CO}, K) = 0, 2 obtained from the $K = 3$-2 and 1-2 subbands indicated that the fault was inherent in the data, and that it most likely arose from a small systematic error in the line position measurements of the R branch relative to the Q branch in the $K = 3$-2 subband. Thus in the final fit, we allowed a constant shift to be added to the $K = 3$-2 R-branch lines and determined its value to be +0.0006 cm^{-1}. The origin listed in Table VII for the $K = 3$-2 subband was determined from the Q-branch lines; it would

TABLE VII

Molecular parameters for CO–Ar (in cm^{-1})[a]

Subband Origins			
K=1-0	2145.2256(1)	K=0-1	2140.4166(1)
K=2-1	2149.4708(1)	K=1-2	2136.0837(1)
K=3-2	2153.4821(2)[b]	K=2-3	2131.9067(1)

Rotational Constants			
		v(CO) = 1	v(CO) = 0
K=0	$\bar{B}$	0.069106(6)	0.069089(6)
	D	0.1968(21) x10^{-5}	0.1913(20)x10^{-5}
	H	-0.403(19) x10^{-9}	-0.463(18) x10^{-9}
K=1	$\bar{B}$	0.068763(6)	0.068776(6)
	D	0.1967(21) x10^{-5}	0.2030(21)x10^{-5}
	H	-0.538(20) x10^{-9}	-0.506(21) x10^{-9}
	B-C	0.004377(3)	0.004328(3)
	d	0.039(8) x10^{-6}	0.087(8) x10^{-6}
	h	0.247(9) x10^{-9}	0.196(10) x10^{-9}
K=2	$\bar{B}$	0.067937(6)	0.067909(7)
	D	0.2537(25) x10^{-5}	0.2369(26)x10^{-5}
	H	-1.299(33) x10^{-9}	-1.545(32) x10^{-9}
	d	-0.705(7) x10^{-6}	-0.639(8) x10^{-6}
	h	-1.638(22) x10^{-9}	-1.747(20) x10^{-9}
K=3	$\bar{B}$	0.066643(10)	0.066643(4)
	D	0.3111(117)x10^{-5}	0.3111 x10^{-5}[c]
	H	-6.61(45) x10^{-9}	-6.61 x10^{-9}[c]
	h	3.41(5) x10^{-9}	3.41 x10^{-9}[c]

[a]Uncertainties in parentheses are one standard deviation from the least-squares fits.
[b]Determined using Q-branch lines; the R-branch gave a value of 2153.4815 cm^{-1} (see text).
[c]Parameters held fixed at the indicated values.

be 0.0006 cm^{-1} lower if determined from the R branch. Small systematic calibration errors such as this can occur in tunable diode laser spectroscopy, because of the way in which line positions are individually measured relative to nearby reference lines.

IV. DISCUSSION AND CONCLUSIONS

The results of Table VII indicate that the rotational constants change very little between the $v_{CO} = 0$ and 1 states. This fact, and more generally the very symmetric nature of the observed spectrum, indicates only a relatively small dependence of the CO–Ar intermolecular potential surface on CO vibrational excitation. The ground state $K = 0$ rotational constant determined for CO–Ar, 0.069089 cm^{-1}, implies an average intermolecular separation of 3.850 Å. The separation of the $K = 1$–0 and 0–1 subband origins, 4.8090 cm^{-1}, gives the sum of the $K = 1$–0 splittings in the $v_{CO} = 1$ and 0 states. This is roughly twice the A-value of the complex (ignoring a-axis centrifugal distortion), so that $A \simeq 2.4$ cm^{-1}.

Unfortunately, there is no way to separate experimentally the $v_{CO} = 1$ and 0 contributions to the a-axis rotational energies without observing parallel ($\Delta K = 0$) transitions. An attempt was made to find the $K = 0$–0 parallel subband in the FT spectrum, but it could not be reliably detected (in the analogous spectrum of CO–Ne, this subband can be seen, though it is very weak compared to the perpendicular subbands). However,

it is reasonable to assume that the CO–Ar $K = 1-0$ separations for $v_{CO} = 1$ and 0 will be in about the same ratio as the corresponding B-values of the CO monomer (0.9912). This implies separations of 2.3939 and 2.4151 cm^{-1} for $v_{CO} = 1$ and 0, respectively. It also gives an overall band origin of 2142.8317 cm^{-1} for the complex, which represents a fairly small shift of -0.440 cm^{-1} from the unperturbed CO monomer origin. It is interesting to note that the vibrational frequency shift for the isoelectronic complex N_2–Ar appears to have a very similar value of about -0.4 cm^{-1} (11).

Having estimated the $K = 1-0$ separations, the origins for the $K = 2$ and 3 stacks of levels with respect to $K = 0$ were found to be 9.0543 and 19.7909 cm^{-1} for $v_{CO} = 1$, and 9.1419 and 19.9581 cm^{-1} for $v_{CO} = 0$. These K-stack origins can then be used to determine the a-axis rotational parameters in the conventional power series, $AK^2 - D_K K^4 + H_K K^6$; the results are listed in Table VIII. We see that the A rotational constant of CO–Ar in its ground vibrational state is found to be 2.4716 cm^{-1}.

The asymmetry splittings of the $K = 2$ levels for both $v_{CO} = 1$ and 0 are inverted with respect to the ordering normally encountered in a prolate asymmetric top molecule. This is shown by the negative values determined for the parameter d for $K = 2$ (Table VII), and it may be verified directly from the experimental data if the $K = 1$ level positions are taken as known from the $K = 1-0$ and $0-1$ subband analyses. Actually, this inversion of the $K = 2$ levels should not be too surprising. We know that $K = 2$ is located at an energy of about 9 cm^{-1} with respect to $K = 0$ at 0 cm^{-1}, and Tennyson and co-workers (2) calculate that the first excited bending state of CO–Ar is located at about 14.3 cm^{-1}. The $K = 2$ levels interact not only with $K = 0$ of the ground state (responsible for the usual asymmetry splitting), but also with $K = 0$ of this bending state. Since the latter $K = 0$ levels are actually considerably closer in energy, the net result is an inversion of the usual ordering of the $K = 2$ doublets.

In the calculation by Tennyson and co-workers (2) of CO–Ar energy levels, the ground state $J = 0$ level is at -84.6 cm^{-1} relative to dissociation, and the highest truly bound rotational state has $J = 35$. Thus our observed J-values of up to 30 in the $K = 1-0$ and $0-1$ subbands are probably fairly close to the dissociation limit. A comparison of the calculations (which are only reported to the nearest 0.1 cm^{-1} and only for J-values of 5 and 10) with our results indicates that their effective B rotational constant is fairly accurate: for example, the calculated interval between $J = 5$ and 10 for $K = 0$ is 5.5 cm^{-1}, and the experimental value is 5.51 cm^{-1}. However, their effective A rotational constant appears to be too large by about 4%: for example, at $J = 10$, the calculated interval between $K = 0$ and $K = 3$ is 28.0 cm^{-1}, whereas the experimental value is 26.67 cm^{-1}.

Altogether in the present analysis, some 370 transitions in the infrared spectrum of CO–Ar have been assigned to six subbands, and molecular parameters have been

TABLE VIII

Approximate a-axis parameters for CO–Ar (in cm^{-1})[a]

	v(CO) = 1	v(CO) = 0
A	2.4526	2.4716
D_K	0.0625	0.0612
H_K	0.0038	0.0037

[a]See text for details.

determined for eight states with $K = 0, 1, 2,$ and 3 and with $v_{CO} = 1$ and 0. However, much remains. A more reliable experimental determination of the a-axis parameters for $v_{CO} = 1$ and 0 will require the observation of weak parallel transitions in the infrared spectrum, or else direct observation of the millimeter wave spectrum of the complex (for example, the $K = 1$–0 Q branch, which will occur in the 70 to 73 GHz region).

Examination of the FT spectrum shows that only a small fraction of the total number of lines has been accounted for. Many of the remaining lines must arise from transitions involving excited bending states of the complex, and the identification of the first excited bending state would be the most important next step in our understanding of the CO–Ar complex. Excited van der Waals stretching states will also be important; Tennyson and co-workers (2) calculate the first such state to lie at about 24.2 cm^{-1}. Theory (2) also shows that the identities of the vibrational states rapidly become confused as the bend and stretch are excited, which serves as a reminder that CO–Ar cannot be treated simply as a normal semirigid molecule, especially in its excited states. An understanding of the whole spectrum will require detailed calculations based on a realistic intermolecular potential energy surface, similar to those of (2), but more precise and complete.

RECEIVED: December 9, 1991

REFERENCES

1. A. DE PIANTE, E. J. CAMPBELL, AND S. J. BUELOW, *Rev. Sci. Instrum.* **60**, 858–862 (1989).

2. J. TENNYSON, S. MILLER, AND B. T. SUTCLIFFE, *J. Chem. Soc. Faraday Trans. 2* **84**, 1295–1303 (1988); see also S. C. FARANTOS AND J. TENNYSON, *in* "New Concepts in Physical Chemistry" (L. S. Cederbaum *et al.*, Eds.), pp. 195–206, Reidel, Dordrecht, 1988.

3. K. MIRSKY, *Chem. Phys.* **46**, 445–455 (1980).

4. S. W. SHARPE, R. SHEEKS, C. WITTIG, AND R. A. BEAUDET, *Chem. Phys. Lett.* **151**, 267–272 (1988).

5. S. W. SHARPE, Y. P. ZENG, C. WITTIG, AND R. A. BEAUDET, *J. Chem. Phys.* **92**, 943–958 (1990).

6. Y. P. ZENG, S. W. SHARPE, D. REIFSCHNEIDER, C. WITTIG, AND R. A. BEAUDET, *J. Chem. Phys.* **93**, 183–196 (1990).

7. S. W. SHARPE, D. REIFSCHNEIDER, C. WITTIG, AND R. A. BEAUDET, *J. Chem. Phys.* **94**, 233–238 (1991).

8. A. R. W. MCKELLAR, *J. Chem. Phys.* **92**, 3261–3277 (1990); A. R. W. MCKELLAR AND J. SCHAEFER, *J. Chem. Phys.* **95**, 3081–3091 (1991).

9. A. R. W. MCKELLAR, *Chem. Phys. Lett.* **186**, 58–64 (1991).

10. A. R. W. MCKELLAR, *in* "Spectral Line Shapes, Vol. 6" (L. Frommhold and J. W. Keto, Eds.), A.I.P. Conference Proceedings 216, pp. 369–383, American Institute of Physics, New York, 1990.

11. See Fig. 6 of A. R. W. McKellar, *J. Chem. Phys.* **88**, 4190–4196 (1988).