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Spectra in the vacuum ultraviolet region of CO in gaseous and solid phases and dispersed in solid argon at 10 K

Hsiao-Chi Lu¹, Hong-Kai Chen¹, Bing-Ming Cheng¹, Yu-Ping Kuo² and J F Ogilvie³

¹ National Synchrotron Radiation Research Center, 101 Hsinn-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan

² Department of Applied Chemistry, Chia Nan University of Pharmacy and Science, Tainan, Taiwan

³ Escuela de Quimica, Universidad de Costa Rica, Ciudad Universitaria Rodrigo Facio, San Pedro de Montes de Oca, San Jose 2060, Costa Rica

E-mail: bmcheng@nsrrc.org.tw and ogilvie@cecm.sfu.ca

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Abstract

With radiation in the region 104–170 nm from a synchrotron and dispersed with a grating monochromator at spectral resolution 0.02–0.03 nm, we measured absorption spectra of ¹²C¹⁶O in the gaseous phase at 303 K and in the solid phase at 10 K, and dispersed in solid argon at molar ratios Ar:CO = 10, 50 and 250 and at 10 K. We assign observed spectral features to transitions to electronic states A ¹Π, B ¹Σ⁺, C ¹Σ⁺ and E ¹Π from the ground state X ¹Σ⁺. Vibrational progressions are discernible for all these systems of CO in the gaseous phase, but for only the system A—X for CO in the pure solid phase of CO or a dispersion in solid argon; for all condensed phases, multiple series of features are deducible in this vibrational structure.

1. Introduction

Carbon oxide, CO, has long been a popular subject of spectral examination. For instance, it was the first diatomic molecular species for which infrared absorption due to its fundamental vibration-rotational band was measured for a gaseous sample in the mid-infrared region (Angstrom 1889). Gaseous CO is normally transparent in the visible or ultraviolet regions because all electronically excited states have great energies, consistent with the fact that CO is the most strongly bound, electrically neutral diatomic molecular species; being convenient for physico-chemical experiments, this stable compound has, however, attracted numerous investigations in the vacuum ultraviolet region, and beyond, for both neutral and ionized states. Work reported before 1977 was summarized by Huber and Herzberg (1979); a discussion of

the nature of electronic states and curves for potential energy were reported by Tilford and Simmons (1972). The electronically excited states most investigated are those of the least energy in the singlet and triplet manifolds, A ${}^{1}\Pi$ and $a {}^{3}\Pi$, respectively. Transitions from the latter state, which is metastable with a lifetime ~5 ms (Lawrence 1972), to or from the ground electronic state are weak, having an oscillator strength $f \sim 10^{-7}$ (Nasson and Nicholls 1971), but are nevertheless detectable in both the gaseous phase (Taylor and Setser 1973) and for CO dispersed in solid noble gases (Fournier *et al* 1980). In contrast, to state A ${}^{1}\Pi$ from the electronic ground state, there is an intense spectrum farther into the vacuum ultraviolet region, with an oscillator strength $f \sim 0.2$ for the entire system or $f_{0,0} \sim 0.0165$ for the origin band (Chan *et al* 1993); this system has attracted much attention for both its general properties and particular perturbations peculiar to a state ${}^{1}\Pi$ (Haridass *et al* 1994).

Quantitative spectral investigation in the vacuum ultraviolet region suffered traditionally from lack of both a convenient source of continuous radiation for absorption experiments and detectors that yield a linear signal. The development of tunable lasers that operate in this region has enabled a renewed attack on quantitative spectrometry; for instance, oscillator strengths of bands in the same system A—X of CO have been measured up to v' = 21 (Stark *et al* 1998), yielding $f_{21,0} \sim 10^{-7}$. Use of lasers in the extreme ultraviolet region has allowed measurement of transitions to highly excited states of CO (Levelt *et al* 1992) beyond the range in which standard optical materials are transparent, and also of Q branches in band 0,0 of system E—X with a great resolution (Cacciani and Ubachs 2004). The availability of an electron synchrotron as a source of continuous and intense radiation over a broad range has proved a further boon to such investigations; for the same system a further band is measurable before interference from other systems, yielding $f_{23,0} \sim 4 \times 10^{-8}$ (Eidelsberg *et al* 1999).

Although infrared spectra of CO in both emission and absorption, and even Raman scattering, in vibrational or vibration-rotational transitions have been measured for samples under diverse conditions in gaseous, liquid and solid states of aggregation, few reports of spectra in the vacuum ultraviolet region have appeared for other than gaseous samples. As this chemical species is important and prominent in spectra of diverse environments and for temperatures over a great range, both terrestrially and extraterrestrially, we have employed radiation from a synchrotron to investigate absorption spectra of CO in three states of aggregation, namely the gaseous phase at 303 K, the solid phase and dispersions in solid argon at molar ratios Ar:CO = 10, 50 and 250 at 10 K. Our spectral range covers from the onset of intense absorption to the limit of transparency of optical crystal LiF, which thus enables measurements pertaining to four intense systems of gaseous CO. A comparison of those spectral features reveals information about the sensitivity of molecular properties to the environment of the carrier molecules.

2. Experiments

We measured absorption spectra of gaseous and condensed samples in the vacuum ultraviolet region with a double-beam absorption apparatus. The radiation from a 'high-flux' beam line of a storage ring (1.5 GeV) at the National Synchrotron Radiation Research Center in Taiwan was dispersed with a cylindrical-grating monochromator (focal length 6 m). The wavelengths were calibrated with absorption lines of Xe (Yoshino and Freeman 1985), CO (Tilford *et al* 1965, Simmons *et al* 1969), O₂ (Yoshino *et al* 1993) and NO (Lagerqvist and Miescher 1958, Engleman *et al* 1970, Murray *et al* 1994, Yoshino *et al* 1998). A small fraction of the light beam was reflected from a LiF crystal plate placed at an angle 45° to the beam line before the gas cell or cold target, passed one additional LiF window, and then impinged onto a glass window coated with sodium salicylate. The photoluminescent signal therefrom that was subsequently

detected with a photomultiplier tube (Hamamatsu R943-02) in a photon-counting mode was employed for normalization.

For absorption by a gas, the light transmitted through the beam splitter (LiF) passed a cell containing the sample equipped with two end windows (LiF), and impinged onto a window (glass, coated with sodium salicylate); the length of optical path in the gas cell is 0.0847 m. The density of the gas was determined from the pressure recorded with a capacitance manometer (MKS, Baratron) and the temperature was monitored with a thermocouple.

For measurements of absorption spectra of a sample in a condensed phase, a cryostat replaced the gas cell. A gaseous sample was deposited onto a rotatable window (LiF) maintained at 10 K. This window was set to face the gas inlet port. Radiation from the synchrotron then intersected this window at an angle near 45° ; the transmitted light impinged onto a window (glass, coated with sodium salicylate) from which the converted visible light was measured with another photomultiplier. The gaseous mixtures were prepared according to standard manometric procedures in an ultra-high vacuum system designed for that purpose. The rate of deposition was regulated in a range/nmol s⁻¹ [7.4, 220] and monitored with a flow transducer. The duration of deposition was typically 180–480 s. CO (Matheson, specified purity 99.99%) and Ar (Matheson, specified purity 99.999%) were used directly without further purification.

Spectra were analysed with software (Microcal Origin 6.0 and Galactic Grams 32) that enabled the conversion of points or curves defining the spectra into areas of spectral lines and deconvolution of complicated line shapes into components of mixed Gaussian and Lorentzian profiles; to characterize each component, this method yielded a wave number of maximum absorption, stature (net maximum absorbance relative to interpolated base line) and width of component at half maximum net absorbance, and its integrated area.

3. Analysis of spectra

3.1. Gaseous CO

In table 1, we list features of a spectrum in figure 1, plotted as absorbance versus wave number, of gaseous CO at pressure 103 Pa assigned to vibrational progressions in four systems; all features are attributed to transitions originating in the electronic and vibrational ground state to various vibrational states within four electronically excited states. The resolution for our measurements in figure 1 is constant at ~0.02 nm, which corresponds to ~8 cm⁻¹ at 63 000 cm⁻¹, ~10 cm⁻¹ at 70 500 cm⁻¹, increasing to ~18 cm⁻¹ at 95 000 cm⁻¹. Rotational structure was thus not quite resolvable, but bands in the system A—X showed the presence of heads in R and Q branches and strongly degraded P branches. Each feature in the other three systems seemed to possess a double maximum indicative of envelopes of unresolved P and R branches. We estimated the total area of these composite features and the centre, G_v , of each unresolved rotational band. These data appear, with differences ΔG_v of wave numbers between adjacent features within a particular progression, in table 1; all values are appropriately rounded for display. The values for areas have a merely relative significance, but are applicable throughout the spectral region.

A weighted fit of apparent band centres G_v in the system A—X according to table 1 to a polynomial in $v + \frac{1}{2}$ with coefficients Y_k^A yielded the following formula, applicable up to v = 15,

$$G_{\rm v}/\rm{cm}^{-1} = (63\,993.0\pm1.8) + (1513.14\pm0.57)\left(v'+\frac{1}{2}\right) - (17.047\pm0.036)\left(v'+\frac{1}{2}\right)^{2};$$
(1)



Figure 1. Absorption spectrum of gaseous CO at 303 K; pressure 103 Pa, length 0.0847 m of optical path, resolution and scan step 0.02 nm.

Table 1. Wave numbers of bands, differences of wave numbers between adjacent bands in a particular vibrational progression and areas of bands in four systems of gaseous $^{12}\mathrm{C}^{16}\mathrm{O}.$

v'	$G_{\rm v}/{\rm cm}^{-1}$	$\Delta G_{ m v}/{ m cm}^{-1}$	Area/cm ⁻¹	
System A—X				
0	64744		84	
1	66 2 28	1485	88	
2	67 669	1440	93	
3	69079	1410	81	
4	70453	1374	91	
5	71 800	1346	62	
6	73111	1311	79	
7	74 383	1272	45	
8	75 623	1240	37	
9	76828	1206	29	
10	77 993	1164	21	
11	79 140	1147	19	
12	80 244	1104	11	
13	81 316	1072	4	
14	82 347	1030	2	
15	83 320	974		
System B—X				
0	86926		44	
1	88 999	2073	26	
2	90991	1991	9	
System C—X				
0	91 929		182	
1	94 088	2159	55	
System E—X				
0	92936		153	
1	95 092	2156	35	



Figure 2. Absorption spectrum of solid CO at 10 K; the rate of deposition is 7.4 nmol s⁻¹, period of deposition 90 s, resolution 0.03 nm, scan step 0.1 nm.

the standard deviation of this fit is 2.3 cm⁻¹, comparable with the spectral resolution. Adding to the constant, Y_0^A , the residual vibrational energy of electronic state X (Ogilvie *et al* 2002), we obtain (65075.4 ± 1.8) cm⁻¹, for comparison with $T_e = 65075.77$ cm⁻¹ (Huber and Herzberg 1979); $v_{0,0}^A = 64744$ cm⁻¹ in table 1 is to be compared with 64748.48 cm⁻¹ (Huber and Herzberg 1979), and the coefficients in formula 1 with $Y_1^A = 1518.24$ cm⁻¹ and $Y_2^A = -19.40$ cm⁻¹ (Huber and Herzberg 1979).

For the system B—X, only two upper vibrational states are reported by Huber and Herzberg (1979), with their difference 2082.26 cm⁻¹, compared to our difference 2073 cm⁻¹. In our spectra, a third feature at 90 991 cm⁻¹ appears clearly to belong to the same progression, in agreement with a preceding observation (Eidelsberg *et al* 1999), yielding $T_e = 86\,940$ cm⁻¹, $Y_1^B = 2155$ cm⁻¹ and $Y_2^B = -41$ cm⁻¹, for comparison with 86 945.2, 2112.7 and -15.2 cm⁻¹ estimated indirectly from isotopic data (Huber and Herzberg 1979), respectively. For each of systems C—X and E—X, we observe only two upper vibrational states, with differences $\Delta G^C = 2159$ cm⁻¹ and $\Delta G^E = 2156$ cm⁻¹ compared to literature values 2146 cm⁻¹ and 2154 cm⁻¹, respectively (Huber and Herzberg 1979). The origin bands are reported at $v_{0,0}^C = 91\,919.15$ cm⁻¹ (Huber and Herzberg 1979) and $v_{0,0}^E = 92\,929.99$ cm⁻¹ (Cacciani and Ubachs 2004); our values $T_e^C = 91\,931$ cm⁻¹ and $T_e^E = 92\,940$ cm⁻¹ compare with 91\,916 cm⁻¹ (Huber and Herzberg 1979) and 92\,929.9285 cm⁻¹ (Cacciani and Ubachs 2004), respectively.

3.2. Solid CO

Shown in figure 2, the spectrum of pure solid CO at 10 K exhibits lines in a series near the vibrational progression in the system A—X of gaseous CO, and two further broad and overlapping lines in regions corresponding to systems B—X, and likely together C, E—X; essential features of these lines—wave numbers, their differences and areas—are summarized in table 2. Scrutiny of the first series reveals that several lines appear to have composite structure, best described as a shoulder on the side of a line at greater wave number; in this way a second series, but having only four members, was deduced. We fitted these lines with mixed Gaussian and Lorentzian profiles because such a combination appeared to yield a fit with

<i>v'</i>	G_{v}	$\Delta G_{\rm v}$	Width	Area	G_{v}	$\Delta G_{\rm v}$	Width	Area
System A—X								
0	63 880		790	1510	64 350		340	130
1	65 340	1460	630	1160	65930	1580	580	760
2	66 890	1550	560	970	67419	1490	550	870
3	68 5 1 0	1620	700	1310	68910	1490	490	640
4	70120	1610	670	950				
5	71480	1360	570	810				
6	72770	1290	520	440				
7	74 030	1260	500	250				
8	75 290	1250	470	110				
9	76490	1200	540	90				
10	77680	1190	480	30				
11	78 790	1110	550	20				
12	80 000	1210	280	5				
System B—X								
-	88 200	4200	2100					
Systems E, C—X								
	92 2 50	6600	3300					

Table 2. Characteristics/cm⁻¹ of spectral features of ${}^{12}C^{16}O$ in a solid phase at 10 K.

satisfactorily small residuals, but the fraction of Lorentzian component is generally small; the fits were free in a sense that only evident shoulders were entered as trial lines with subsidiary maxima. A summary of all these results, with widths and relative areas, appears in table 2.

A weighted fit of features, according to table 2, in the dominant progression attributed to the system A—X of solid ¹²C¹⁶O to a quadratic function of $v' + \frac{1}{2}$ up to v' = 12 produces this result,

$$G_{\nu}/\mathrm{cm}^{-1} = (62\,890\pm50) + (1683\pm20)\left(\nu'+\frac{1}{2}\right) - (26.2\pm1.5)\left(\nu'+\frac{1}{2}\right)^{2};\tag{2}$$

the standard deviation of this fit is 43 cm^{-1} , dictated by the breadth of the lines as tabulated. By comparison with formula (1), the constant term indicates that condensation of CO from the gaseous phase at a small density to a solid state of aggregation causes a shift ~1100 cm⁻¹ to smaller wave number, but coefficients Y_1^A and Y_2^A acquire enhanced magnitudes for this solid sample. The comparison is nevertheless sufficiently close that there can be no doubt that this progression in the solid phase is analogous to, and corresponds to, that in the system A—X for a gaseous sample.

In contrast, the broad line with maximum absorption near $88\,000\,\mathrm{cm}^{-1}$ for solid CO seems shifted to greater wave number than the origin of system B—X of gaseous CO. A second broad feature, discernible only on fitting the profile, has its centre almost midway between the origins of systems C—X and E—X; on this basis, attribution to both electronic transitions might seem appropriate, but interactions between adjacent molecular sites within the lattice might greatly perturb these electronic states so that such an assignment becomes at least questionable.

3.3. CO dispersed in solid Ar

We measured, in absorption, spectra of CO dispersed in solid argon at 10 K at molar ratios Ar:CO = 10, 50 and 250. Just as for pure solid CO, features of lines attributable to a vibrational progression of CO molecules in electronically excited state A ¹ Π exhibit a composite structure; essential features—wave numbers, their differences and areas—are summarized in table 3.

Table 3. Characteristics/cm⁻¹ of spectral features in the system A ${}^{1}\Pi \leftarrow X {}^{1}\Sigma^{+}$ for ${}^{12}C^{16}O$ dispersed in solid Ar at 10 K.

	Progression A				Progression B				Progression C			
v'	$\overline{G_{\mathrm{v}}}$	$\Delta G_{\rm v}$	Width	Area	$\overline{G_{v}}$	$\Delta G_{ m v}$	Width	Area	$\overline{G_{v}}$	$\Delta G_{\rm v}$	Width	Area
Mol	ar ratio Ar	:CO = 1	0									
0	64 1 30		320	440	63 720	640	270					
1	65 630	1500	370	1010	65 140	1420	390	150				
2	67 090	1470	400	1180	66 6 30	1480	220	60				
3	68 5 10	1420	400	1020	68 070	1440	190	20				
4	69 900	1390	350	690								
5	71 240	1340	330	420								
6	72540	1300	310	250								
7	73810	1270	320	110								
8	75070	1260	290	60								
9	76290	1220	330	35								
10	77470	1170	320	20								
11	78 630	1160	340	10								
Mol	ar ratio Ar	:CO = 5	0									
0	64070		220	280	63 750		520	80	64 270		350	100
1	65 570	1500	250	690	65 170	1420	300	50	65 840	1570	260	120
2	67 0 10	1430	230	570	66 650	1480	190	25	67 190	1350	350	350
3	68 4 40	1430	240	610	68 100	1450	120	10	68 670	1480	290	180
4	69810	1380	210	390					70000	1330	300	190
5	71 150	1340	200	220					71310	1310	300	160
6	72480	1330	220	180					72710	1400	270	40
7	73750	1270	200	60					73 890	1190	370	60
8	75000	1250	200	30					75110	1220	380	30
9	76220	1210	190	20					76380	1270	460	20
10	77 430	1210	300	20								
11	78 550	1120	480	10								
Mol	ar ratio Ar	:CO = 2	50									
0	64 060		212	200	64 320		320	40				
1	65 560	1500	230	450	65 850	1530	240	60				
2	67 000	1440	210	410	67 220	1370	340	140				
3	68 4 20	1420	220	380	68 670	1460	290	90				
4	69 800	1380	200	240	70 000	1330	350	90				
5	71 140	1340	190	140	71 320	1310	360	90				
6	72460	1320	200	90	72 690	1370	400	50				
7	73740	1280	200	50	73 950	1270	320	20				
8	74990	1250	180	20	75 180	1220	450	20				
9	76210	1220	210	20	76470	1300	160	5				
10	77410	1200	250	10								
11	78 560	1150	300	15								

An analysis of the spectrum shown in figure 3 indicates that, at molar ratio 10, besides a prominent progression, denoted by 10A, comprising 12 members, four members of a subsidiary progression 10B appear at smaller wave number. An analysis of the spectrum shown in figure 4 indicates that, at the molar ratio 50, three progressions are discernible: the main progression 50A has 12 members, a short progression 50B at a smaller wave number has only four members, but another progression 50C at a larger wave number has 10 members.



Figure 3. Absorption spectrum of CO dispersed in solid Ar at molar ratio Ar:CO = 10 and at 10 K; the rate of deposition is 89 nmol s^{-1} , period of deposition 120 s, resolution 0.03 nm, scan step 0.1 nm.



Figure 4. Absorption spectrum of CO dispersed in solid Ar at molar ratio Ar:CO = 50 and at 10 K; the rate of deposition is 220 nmol s⁻¹, period of deposition 180 s, resolution 0.03 nm, scan step 0.1 nm.

An analysis of the spectrum shown in figure 5 indicates that, at molar ratio 250, only two progressions are detectable: the major one 250A has 12 members and a minor one 250B 10 members at a larger wave number.

For any sample of CO dispersed in Ar, no progression coincides with either for solid CO, but progressions 250A and 50A essentially coincide: a barely significant shift (13 ± 7) cm⁻¹ is minuscule relative to widths ~200 cm⁻¹ deduced for individual components. Those progressions 250A and 50A hence appear to share a common, significant and



Figure 5. Absorption spectrum of CO dispersed in solid Ar at molar ratio Ar:CO = 250 and at 10 K; the rate of deposition is 220 nmol s⁻¹, period of deposition 480 s, resolution 0.03 nm, scan step 0.05 nm.

consistent shift \sim (75 ± 15) cm⁻¹ from progression 10A. Progressions 250B and 50C appear to coincide: their differences of wave number between corresponding members are (30 ± 34) cm⁻¹. As both these progressions suffer from being subsidiary, wave numbers of their lines are less satisfactorily characterized than for the corresponding main progressions: the uncertainty of measurement of wave numbers of lines in progression 250B is about ten times that of lines in 250A. There is a consistent but small shift, (28 ± 5) cm⁻¹, between corresponding lines in progressions 50B and 10B, and the widths of lines in both sets appreciably decrease from ~600 cm⁻¹ at v' = 0 to ~150 cm⁻¹ at v' = 3, which is the last discernible member of each series. The shift between progressions 10A and 10B is (450 ± 30) cm⁻¹, comparable with the shift (360 ± 30) cm⁻¹ between progressions 50A and 50B. The shifts between progressions 50A and 50C and between 250A and 250B are practically identical, (225 ± 35) cm⁻¹.

A weighted fit of wave numbers of lines in progression 10A yields

$$G_{\rm v}/\rm{cm}^{-1} = (63\,378\pm9) + (1527\pm4)\left(v'+\frac{1}{2}\right) - (17.7\pm0.3)\left(v'+\frac{1}{2}\right)^2;\tag{3}$$

the standard deviation of this fit is 9.3 cm⁻¹. A similar weighted fit for progression 50A yields

$$G_{\rm v}/\rm{cm}^{-1} = (63\,327\pm6) + (1517\pm3)\left(v'+\frac{1}{2}\right) - (16.8\pm0.2)\left(v'+\frac{1}{2}\right)^2;\tag{4}$$

the standard deviation of this fit is 7.0 cm⁻¹. For progression 250A a similar fit yields

$$G_{\rm v}/\rm{cm}^{-1} = (63\,327\pm4) + (1511\pm1.5)\left(v'+\frac{1}{2}\right) - (16.2\pm0.1)\left(v'+\frac{1}{2}\right)^2;\tag{5}$$

the standard deviation of this fit is 3.1 cm^{-1} . The decreasing standard errors of parameters for increasing molar ratio reflect the narrowing of lines in these main progressions; the coefficients of $(v'+\frac{1}{2})$ and $(v'+\frac{1}{2})^2$ are otherwise almost indistinguishable. The identical constant terms for progressions 50A and 250A and the shift ~50 cm⁻¹ of each of these from that of progression 10A is consistent with the deductions drawn above on the basis of differences of wave numbers of respective lines in these series.

Molar ratio $Ar:CO = 10$			Molar ratio $Ar:CO = 50$			Molar ratio $Ar:CO = 250$		
ĩ	Width	Area	ĩ	Width	Area	ĩ	Width	Area
						84 800	2200	70
			88 550	2200	370	88 300	800	80
						89 000	800	60
92 200 92 800	1100 9200	260 2900	92 300	900	280	92 300	900	250
			95 800	5500	1350	95 200	4900	1100

Table 4. Characteristics/cm⁻¹ of spectral features discerned in the region 80 000–96 000 cm⁻¹ for ¹²C¹⁶O dispersed in solid Ar at 10 K.

Summarized in table 4, the spectrum of CO in Ar at molar ratio 10 exhibits a broad feature extending past the upper limit of measurement, and a less broad line, centred about 92 250 cm⁻¹, above it; the apparent centres of these two features are almost the same. At molar ratios 50 and 250, multiple features, but still broad, appear in this wide region, apparently unrelated to the vibrational structure. Fits of these features indicate that their apparent centres might lie beyond the limit of measurements; in that region there might be also some contribution to absorption from host Ar.

4. Discussion

Our measurements of the spectrum of gaseous CO in the region of four systems involving electronically excited singlet states provide new quantitative data about spectral properties of these states. The partially resolved rotational envelopes of particular vibrational bands in each observed system are consistent with traditional assignments of electronic transitions (Tilford and Simmons 1972). Apart from the additional member of the vibrational progression of system B—X, from comparison of the total integrated intensities of systems B, C and E—X with that of system A—X for which we accept $f \sim 0.18$ (Chan et al 1993), we estimate oscillator strengths of the other systems to be for B-X, $f \sim 0.019$; for C—X, $f \sim 0.057$, and for E—X, $f \sim 0.045$, with relative uncertainties less than 5%. The oscillator strength of an individual band within a system stands in proportion to the total oscillator strength of that system as the area of that band to the total area. Such results are practicable because the synchrotron produces radiation essentially continuous in wavelength and because our detector is operated in a linear regime. Absorbance in our spectra is, however, not linearly proportional to the concentration of absorber because the pressure, 103 Pa, for our measurements was much greater than an upper limit, 0.267 Pa, appropriate to a linear regime (Lee and Guest 1981); the length, 0.070 m, of the optical path of the sample in those measurements (Lee and Guest 1981) is comparable with our length, 0.0847 m. For that reason our integrated areas for gaseous samples are not reliably comparable with calculated Franck–Condon factors; despite this reservation our oscillator strengths above fall roughly in the ranges from the literature with values for B—X, $f \sim 0.0052 - 0.0153$; for C—X, $f \sim$ 0.013 - 0.122, and for E—X, $f \sim 0.018 - 0.075$ (Chan *et al* 1993). Because these problems of limited resolution do not affect spectral features of condensed phases for which widths of lines are much greater than for gaseous samples, the ratios of oscillator strengths would be much more reliable, but for those condensed phases the spectral features are not readily distinguishable according to separate excited states other than state A.

By comparison of our spectra of CO dispersed in solid Ar at 10 K with infrared spectra of samples prepared under similar conditions (Han and Kim 1997), we tentatively

attribute progressions 250A and 50A to CO molecules with only Ar as nearest neighbours, and progressions 250B and 50C to CO molecules with at least another CO molecule as a nearest neighbour. At molar ratio Ar;CO = 250, on a basis of a CO molecule occupying a substitutional site in an approximately crystalline lattice in which the order over at least a short range resembles that in a perfect crystal, one expects a priori about 92% of CO molecules to have only Ar as a nearest neighbour (Jackson and Montroll 1958), or a ratio \sim 11:1 of fully isolated molecules to others. That estimate must be an upper limit because ideal conditions consistent with that purely statistical value are unlikely to prevail under actual experimental conditions in which reorganization, subject to intermolecular interactions, at the surface of the growing deposit occurs to an unknown extent; the ratio of total areas of lines in series 250A and 250B is \sim 4:1. The great breadth of spectral features for solid samples in regions corresponding to transitions to states B, C and E in the gaseous phase indicates a strong electronic coupling between molecules of CO, or even possibly between CO and Ar, at those large energies, even though the vibrational wave numbers and bond lengths of the free molecules alter only slightly as a result of those transitions. In contrast, for the system A—X the electronic excitation appears to be largely localized within individual molecules, although the slight variation of vibrational coefficients Y_k^A depending on conditions in solid phases indicates a significant perturbing influence of the environment; this weak interaction of an absorbing molecule with the environment occurs despite the bond length of CO increasing significantly, and presumably likewise the effective molecular volume, accompanying this electronic transition.

For system A—X, Franck–Condon factors for the vibrational series 0–0 up to 9–0 on the basis of spectral parameters for free molecules are calculated to be 0.122, 0.227, 0.235, 0.180, 0.113, 0.063, 0.032, 0.015, 0.0069, 0.0030. For the sum of integrated areas of spectral lines for each excited vibrational state as a fraction of the total area up to v' = 7, there is rough agreement between these values and those in the preceding list, but then the calculated values diminish much more rapidly with increasing v' than our experimental values. To the extent that our relative intensities are not distorted by the effects of saturation in the absorption spectrum, this discord implies a significant departure of the radial function for the electronic transition moment from a constant value. For pure solid CO, there is a similar trend of agreement. Because the vibrational parameters in formulae (2) and (3) differ significantly from those in formula (1), we do not expect close agreement between Franck-Condon factors calculated on a basis of data for the free molecule, as in the gaseous phase, and those from experiment for molecules in the solid phase. The principal vibrational parameter Y_1^A for state A has a value (1513.14 ± 0.57) cm⁻¹ for the gaseous sample, according to our measurements, but this value increases significantly to (1683 \pm 20) cm⁻¹ for pure solid CO; this disparity of Y_1^A between samples of CO in the gaseous and pure solid phases implies that the confining environment of a molecule in the latter condition distorts the internal force field of a molecule reflected in the potential-energy function. In contrast, the values/cm⁻¹, namely 1527 ± 4 , 1517 ± 3 and 1511 ± 1.5 according to formulae (3)–(5) respectively, of this parameter for CO dispersed in solid Ar are comparable with the value $Y_1^A = 1513.14 \text{ cm}^{-1}$ for the gaseous phase.

5. Conclusion

We have reported for the first time spectra of CO in a solid phase and dispersed in solid argon at 10 K measured in absorption in a spectral region $60\,000-96\,000\,\mathrm{cm^{-1}}$, and have compared the features of these states of aggregation with those of the gaseous phase. Just as for infrared spectra of both solid CO and CO dispersed in solid argon, multiple features are discernible for a given vibrational transition between electronic states X and A, but transitions to other excited states B, C and E are not readily distinguishable because the spectral features have large widths.

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