Note

Neon matrix isolation spectroscopy of CO_2 isotopologues

Lei Wan, Lei Wu, An-Wen Liu, Shui-Ming Hu [*]

Department of Chemical Physics, Hefei National Laboratory for Physical Sciences at Microscale, University of Science and Technology of China, Number 96, Jin Zhai Lu (Road), Hefei, Anhui 230026, China

A R T I C L E   I N F O

A B S T R A C T

The solid neon matrix isolated spectrum of CO_2 are recorded in the 2–5 μm region. Natural and ^{13}C or [18]O enriched CO_2 samples were used and the $nv_1 + v_3$ (n = 0, 1, 2) series bands of different CO_2 isotopologues have been observed. The solid neon matrix shift due to Fermi-resonance of bands within the same vibrational polyad is analyzed.

© 2009 Elsevier Inc. All rights reserved.

The spectrum of carbon dioxide have been extensively studied. The matrix isolation spectroscopy of CO_2 have been reported in solid N_2 [1,2], O_2 [3], Ar [1,2,4], Kr [5], p-H_2 [6] and in helium droplet [7].

The matrix shift and matrix splitting provide a measure of the intermolecular interactions between host matrices and guest molecules. The strong fundamental anti-symmetric stretching band v_3 of CO_2 has been most extensively studied, but the overtones are less considered because such bands are much weaker and often hard to be identified from the bands of other contaminations in the sample. Moreover, complicated spectroscopic structure can often be found for a single vibrational band of the dopant. The structure arises from matrix crystal field, dopant aggregations, different substitutional sites in matrices, vibrational band interactions and rotational structures, or from the isotopic effect. These effects also make it difficult to assign the overtone bands. By comparing the spectra from different isotope-enriched samples, we have successfully studied the overtones of N_2O in solid neon and p-H_2 matrices [8,9]. The relatively small matrix effect of solid neon resulted in regular matrix shifts of vibrational bands [8]. In this work, we investigate the infrared spectra of CO_2 embedded in neon matrices, from the strong fundamental v_3 band to the much weaker overtones extended to the 2 μm region. The vibrational assignments are confirmed by a systematic study of different isotopologues of CO_2.

Natural and isotope concentrated CO_2 samples were used in the present study. The natural sample was bought from Nanjing Special Gas Co. The ^{13}C enriched and [18]O enriched samples were purchased from Icon Services Inc. The isotopic abundance of each sample was determined by the infrared spectroscopy and also the photo-ionization mass spectroscopy (PIMS) measurements.

The PIMS measurement was carried out in the photochemistry end-station of National Synchrotron Radiation Laboratory (Hefei, China). All these sample was further purified with "thaw–frozen–thaw" procedure before using. Totally 10 different CO_2 isotopologues were studied: $^{12}C^{16}O_2$, $^{16}O^{12}C^{17}O$, $^{16}O^{12}C^{18}O$, $^{17}O^{12}C^{18}O$, $^{12}C^{18}O_2$, $^{13}C^{16}O_2$, $^{16}O^{13}C^{17}O$, $^{16}O^{13}C^{18}O$, $^{17}O^{13}C^{18}O$, and $^{13}C^{18}O_2$. These isotopologues will be noted as CO_2-626, 627, 628, and so on, respectively.

The sample gas was deposited on a BaF_2 substrate through a 0.1 mm diameter pinhole. The distance between the pinhole and the BaF_2 substrate was about 3 cm. The flow rate was controlled at about 27 mmol/h by a mass-flow controller (MKS 1479A). The BaF_2 substrate was attached to the cold head of a closed-cycle cryostat (Janis SHI-4-5). A LakeShore 331S controller was used to control the heating current in a wire attached to the cold head. In this way, the temperature can be adjusted in the range of 4–300 K with 0.2 K accuracy. Typically, the deposition temperature is 4.3 K and the annealing temperature is 10 K. After annealing, the temperature will be again lowered to 4.3 K. The infrared absorption spectra were recorded by a Bruker IFS120HR Fourier-transform spectrometer. The entire optical path was evacuated to avoid the atmospheric absorption. The spectra covering the 700–6000 cm^{-1} region were recorded with proper selections of the light sources (glowbar or tungsten lamp), beam splitters (KBr or CaF_2) and detectors (ℓN_2 cooled MCT or InSb). The adopted spectral resolution was 0.02 cm^{-1}.

The band assignments can be readily made by the comparison with the gas phase band centers of respective isotopologues [10,11]. We have been able to assign the $nv_1 + v_3$ (n = 0, 1, 2) bands in the region 2–5 μm. Parts of the observed spectrum, showing the v_3, $v_1 + v_3$ and $2v_1 + v_3$ band/polyads of the main isotopologue $^{12}C^{16}O_2$ are given in Fig. 1. Fig. 2 shows the strongest band in the $2v_1 + v_3/v_1 + 2v_2 + v_3/4v_2 + v_3$ polyad of $^{12}C^{16}O_2$. The small peaks

---
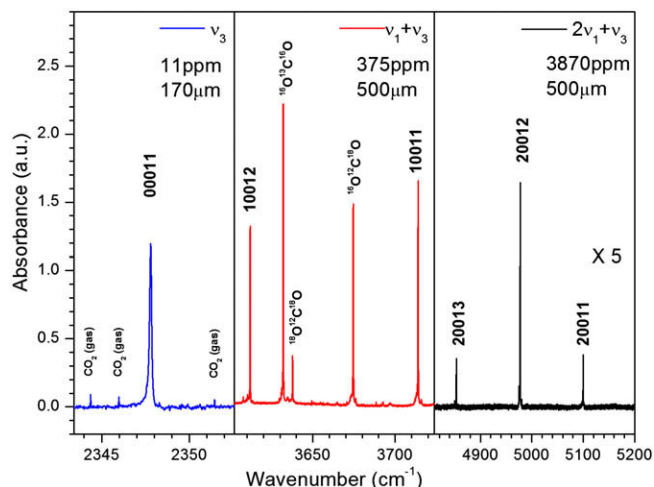
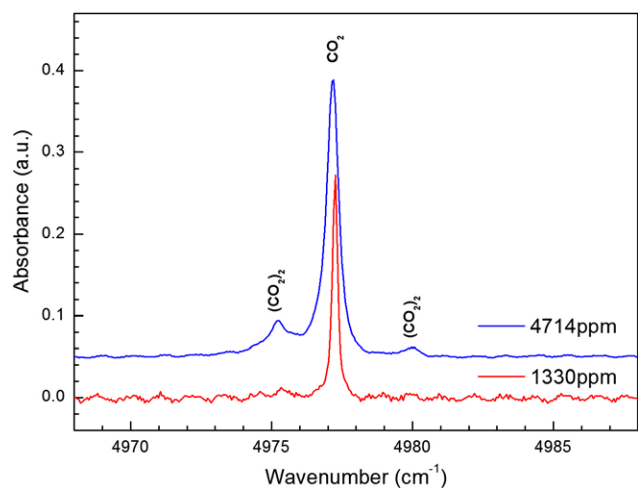**Fig. 1.** The v_3, $v_1 + v_3$ and $2v_1 + v_3$ bands of $^{12}C^{16}O_2$ in solid neon.

Fig. 2. The strongest band in the $2v_1 + v_3$ polyad of $^{12}C^{16}O_2$ in solid neon. Spectrum were recorded after 0.5 mm CO_2/Ne sample had been deposited at 4.3 K.

Table 1
Band shifts of CO_2 isotopologues (in cm^{-1}) in solid neon matrices.

iso.[a]	Vib.[b]	G_v[c]	v_{Ne}	δ_{Ne}[d]	Int.%[e]	Δ[f]
	v_3					
838	$00^0 11$	2247.291	2246.010	−1.281		
738		2255.954	2254.656	−1.298		
638		2265.971	2264.671	−1.301		
637		2274.087	2272.767	−1.320		
636		2283.487	2282.174	−1.313		
828		2314.048	2312.732	−1.316		
728		2322.436	2321.114	−1.322		
628		2332.112	2330.784	−1.328		
627		2340.014	2338.664	−1.350		
626		2349.143	2347.798	−1.345		
	$v_1 + v_3$					
838	$10^0 11$	na	3544.383	na	52	—
	2	na	3447.403	na	48	
638	1	3587.550	3586.717	−0.833	63	−0.885
	2	3490.396	3489.420	−0.976	37	
637	1	3608.559	3607.652	−0.907	64	−0.925
	2	3508.376	3507.419	−0.957	36	
636	1	3632.910	3631.953	−0.958	78	−0.961
	2	3527.738	3526.764	−0.974	22	
828	1	3638.065	3637.666	−0.399	33	−0.871
	2	3525.204	3524.105	−1.099	67	
628	1	3675.133	3674.545	−0.588	47	−0.836
	2	3571.140	3570.087	−1.053	53	
627	1	3693.346	3692.648	−0.698	28	−0.943
	2	3591.251	3590.213	−1.038	72	
626	1	3714.782	3714.000	−0.782	61	−0.871
	2	3612.841	3611.828	−1.013	39	
	$2v_1 + v_3$					
638	$20^0 11$	4925.013	4924.991	−0.022	25	−0.469
	2	4814.570	4813.935	−0.635	57	
	3	4692.179	4691.585	−0.594	17	
636	1	4991.353	4990.971	−0.382	54	−0.524
	2	4887.391	4886.700	−0.691	46	
628	2	4904.860	4904.431	−0.430	68	−0.485
	3	4791.260	4790.658	−0.602	32	
626	1	5099.661	5099.736	0.075	17	−0.520
	2	4977.835	4977.183	−0.652	71	
	3	4853.623	4853.038	−0.585	12	

[a] Notation for the CO_2 isotopologues, i.e. 638 for $^{16}O^{13}C^{18}O$.
[b] Upper state, $v_1 v_2^{\ell_2} v_3 \gamma$, consistent with the HITRAN[12] notations.
[c] Gas phase values, from Refs. [10,11].
[d] Solid neon matrix shift, $\Delta_{Ne} = v_{Ne} - G_v$.
[e] Observed relative band intensity in the vibrational polyad.
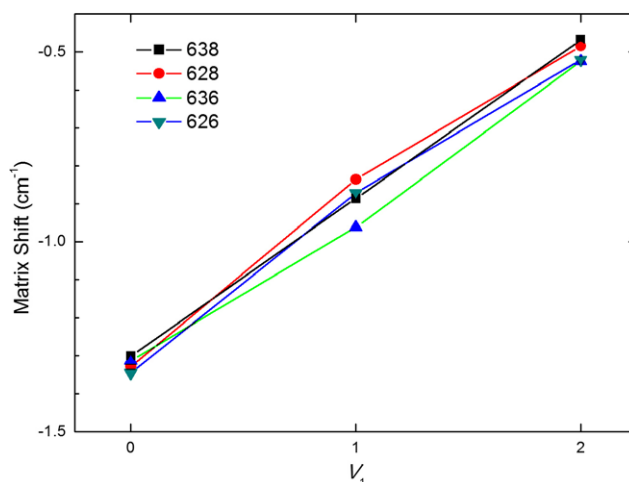[f] Weighted matrix shift of the vibrational polyad.

appear in the spectrum with high CO_2 concentration are attributed to the CO_2 dimer. The assignments and the matrix shifts of different isotopologues of CO_2 are presented in Table 1. As comparison, the vibrational term G_v values of gas phase CO_2 are also given in the table. The vibrational notations follow Ref. [10] and the HITRAN database [12], where a vibrational state is denoted with quantum numbers $v_1 v_2^{\ell_2} v_3 \gamma$. The numbers v_1, v_2, v_3 are the quanta of the symmetric stretching, bending and anti-symmetric stretching vibration modes, respectively. ℓ_2 is the vibrational angular momentum quantum number. γ is the index of the vibrational state within a Fermi-resonance polyad.

For the strong v_3 band, the transitions have been assigned for 10 isotopologues of CO_2. The neon matrix shift of the v_3 band is very close for different isotopologues, which ranges from 1.28 to 1.35 cm^{-1}. However, for the $v_1 + v_3$ and $2v_1 + v_3$ polyads, the matrix shifts change a lot between different isotopologues. The reason can be that the interactions among the vibrational states in the polyad cause mixing of the wavefunctions. The change of the potential energy surface due to the matrix environment will lead the change of wavefunction mixing. As a result, the relative band intensities in a polyad changes in the neon matrices from the gas phase. The relative band intensities as the parts of the whole interacting polyad are also given in Table 1. The values change much from the gas

Fig. 3. The $nv_1 + v_3$ band shifts of several CO_2 isotopologues in solid neon (CO_2 isotopologue notation: 626 for $^{16}O^{12}C^{16}O$, 638 for $^{16}O^{13}C^{18}O$, etc.).

phase ones [10,11]. In the last column of the table, we give the averaged matrix shifts weighted with the relative band intensities

within a polyad. Fig. 3 shows the "weighted matrix shifts" of different isotopologues. We can see that the value changes little from one isotopologue to another. It is clear that the matrix shift values change almost linearly with n for the $n\nu_1 + \nu_3$ ($n = 0, 1, 2$) bands. This "regular" behavior can be an advantage to predict the matrix shifts of molecules in solid neon.

Acknowledgments

References

[1] A. Schriver, L. Schriver-Mazzuoli, A.A. Vigasin, Vib. Spectrosc. 23 (2000) 83–94.
[2] J.A.G. Castano, A. Fantoni, R.M. Romano, J. Mol. Struct. 881 (2008) 68–75.
[3] M. Minenko, M. Vetter, A.P. Brodyanski, H.J. Jodl, Low Temp. Phys. 26 (2000) 699–711.
[4] L.M. Nxumalo, T.A. Ford, J. Mol. Struct. 327 (1994) 145–159.
[5] A. Loewenschuss, A. Givan, Spectrosc. Lett. 10 (1977) 551–558.
[6] S. Tam, M.E. Fajardo, Low Temp. Phys. 26 (2000) 653–660.
[7] K. Nauta, R.E. Miller, J. Chem. Phys. 115 (2001) 10254–10260.
[8] L. Wan, G. Xu, L. Wu, Y. Chen, S.-M. Hu, J. Mol. Spectrosc. 249 (2008) 65–67.
[9] S.-M. Hu, L. Wan, J.-H. Du, G. Xu, W.-P. Deng, L. Wu, S.-X. Tian, Y. Chen, Vib. Spectrosc. 50 (2009) 36–42.
[10] L.S. Rothman, R.L. Hawkins, R.B. Wattson, R.R. Gamache, J. Quant. Spectrosc. Radiat. Transfer 48 (1992) 537–566.
[11] J.-L. Teffo, C. Claveau, A. Valentin, J. Quant. Spectrosc. Radiat. Transfer 59 (1998) 151–164.
[12] L.S. Rothman, D. Jacquemart, A. Barbe, D. Chris Benner, M. Birk, L.R. Brown, M.R. Carleer, C. Chackerian Jr., K. Chance, L.H. Coudert, V. Dana, V.M. Devi, J.-M. Flaud, R.R. Gamache, A. Goldman, J.-M. Hartmann, K.W. Jucks, A.G. Maki, J.-Y. Mandin, S.T. Massie, J. Orphal, A. Perrin, C.P. Rinsland, M.A.H. Smith, J. Tennyson, R.N. Tolchenov, R.A. Toth, J. Vander Auwera, P. Varanasi, G. Wagner, J. Quant. Spectrosc. Radiat. Transfer 96 (2005) 139–204.