

# Infrared absorption spectroscopy of the CO<sub>2</sub>-Ar complex in the 2376 cm<sup>-1</sup> combination band region: The intermolecular bend

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(Received 23 August 1990; accepted 10 September 1990)

The rovibrational absorption spectrum of CO<sub>2</sub>-Ar has been recorded in the 2376 cm<sup>-1</sup> region by using a pulsed, slit nozzle expansion and tunable IR diode laser. The spectrum is ascribed to the 4<sub>0</sub><sup>1</sup>5<sub>0</sub><sup>1</sup> combination band, where  $\nu_4$  corresponds to the asymmetric stretch of the CO<sub>2</sub> moiety and  $\nu_5$  is the intermolecular bend. This combination band is  $\sim 10^2$  times less intense and 27.82 cm<sup>-1</sup> higher in energy than the 4<sub>0</sub><sup>1</sup> fundamental. Effective upper-state rotational constants were determined for this nearly prolate rotor, and the  $\nu_4 + \nu_5$  moments of inertia show a large inertial defect,  $\Delta = 9.48$  amu Å<sup>2</sup>. In planar molecules, this indicates large vibrational amplitude, and reflects inadequacy of the rotational Hamiltonian. From the moments of inertia derived using a Watson Hamiltonian, geometric properties of  $\nu_4 + \nu_5$  can be calculated. The average O-C-Ar angle is 76.9°, while the center-of-mass separation between CO<sub>2</sub> and Ar is 3.60 Å. These values differ from those of the ground state (83.1° and 3.51 Å) and  $\nu_4 = 1$  (83.0° and 3.50 Å). Results are compared with previous work, which used different models and approximations to obtain intermolecular frequencies. In addition, inertial defects were calculated for the ground and vibrationally excited states using a simple normal mode model developed by Herschbach and Laurie, and Oka and Morino. With harmonic force fields, it accounts for most of the inertial defect in the ground and excited states, and yields reasonable  $R$  and  $\theta$  values. However, we conclude that the good agreement between experimental and calculated inertial defects may be fortuitous, since several positive and negative contributions cancel.

## I. INTRODUCTION

Spectroscopic studies of weakly bonded gas phase complexes provide a means of understanding long-range intermolecular forces and energy transfer dynamics.<sup>1</sup> Rare gas (Rg) complexes such as CO<sub>2</sub>-Rg are of interest because the anisotropic intermolecular potential derives from dispersive, i.e., van der Waals, forces. Such interactions generally result in shallow potentials that may support liquid-like motions in which Rg orbits around CO<sub>2</sub>.<sup>2</sup> In addition, binding energies and vibrational frequencies provide a sensitive test for theoretical calculations.

CO<sub>2</sub>-Ar is particularly amenable to IR spectroscopic studies because of the ease with which it can be produced and detected. CO<sub>2</sub> and Ar readily complex to form the dimer, and based on measurements of the ratio of monomer to dimer absorption intensities, we estimate that  $\sim 5\%$  of the CO<sub>2</sub> forms CO<sub>2</sub>-Ar. The large CO<sub>2</sub> IR absorption cross section, which changes little upon formation of the complex, greatly facilitates detection. As in all CO<sub>2</sub>-Rg complexes, CO<sub>2</sub>-Ar is a T-shaped C<sub>2v</sub> molecule with six vibrational normal modes. Four of these are essentially the high frequency modes of the CO<sub>2</sub> moiety, while the two low frequency modes,  $\nu_3$  and  $\nu_5$ , correspond to the intermolecular stretch and bend, respectively; for clarity, we shall sometimes refer to these as  $\nu_s$  and  $\nu_b$ . A pictorial description of the six modes is given in Fig. 1. The nomenclature of Fraser *et al.* is used in labeling these vibrations.<sup>3</sup>

Originally, scattering data and potential surface calculations predicted a T-shaped equilibrium geometry for CO<sub>2</sub>-Ar,<sup>4,5</sup> and this was subsequently confirmed by the radio-frequency and microwave molecular beam electric reso-

nance experiments of Klemperer and co-workers.<sup>6</sup> Structural parameters for various vibrational states are summarized in Table I. From a normal coordinate analysis and the values of the centrifugal distortion constants, Klemperer and co-workers estimated the intermolecular vibra-

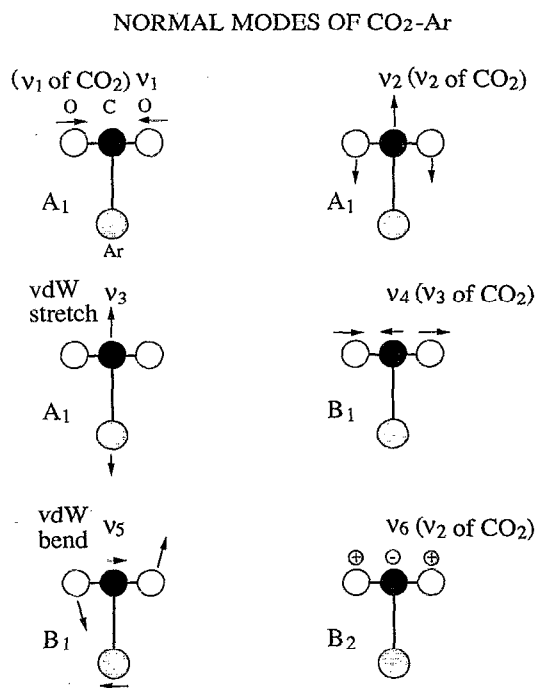


FIG. 1. Pictorial description of CO<sub>2</sub>-Ar normal modes.

TABLE I. Effective and standard moments of inertia (amu Å<sup>2</sup>) for CO<sub>2</sub>-Ar.

	Ground <sup>a</sup>	$\nu_4 = 1^a$	$\nu_4 = 1, \nu_5 = 1$
$I_A^{\text{eff}}$	42.453	42.775	40.891
$I_B^{\text{eff}}$	255.372	255.510	264.918
$I_C^{\text{eff}}$	300.261	300.677	315.284
$\Delta^{\text{eff}}$	2.436	2.392	9.476
$\langle R \rangle$ (Å)	3.51	3.50	3.60
$\langle \theta \rangle$ (deg)	83.1	83.0	76.9
$I_A^0$	42.743	43.113	41.704
$I_B^0$	257.574	257.713	270.239
$I_C^0$	300.243	300.705	313.495
$\Delta^0$	-0.075	0.120	1.552
$\langle R \rangle$ (Å)	3.50	3.51	3.60
$\langle \theta \rangle$ (deg)	84.6	84.8	79.1

<sup>a</sup> Effective moments of inertia taken from Ref. 8. Values of 43.2004 and 43.5439 amu Å<sup>2</sup> were used for the values of the moments of inertia of CO<sub>2</sub> in the ground and excited  $\nu_4$  state, respectively.

tional frequencies to be 37.5(7) and 27.5(2) cm<sup>-1</sup> for  $\nu_s$  and  $\nu_b$ , respectively. Subsequently, the bending mode frequency was changed to  $\omega_b = 38.9(2)$  cm<sup>-1</sup>, following the discovery of an error in the earlier paper.<sup>7</sup>

More recently, high-resolution IR rovibrational spectra of CO<sub>2</sub>-Ar were reported. Randall *et al.*<sup>8</sup> and our group<sup>9</sup> obtained spectra corresponding to excitation from the ground state to  $\nu_4 = 1$ , which is predominantly the asymmetric stretching mode of the CO<sub>2</sub> moiety, as shown in Fig. 1. The vibrational wave functions for the  $\nu_4 = 1$  and ground states belong to  $B_1$  and  $A_1$  representations of the  $C_{2v}$  point group, respectively. Thus, only  $b$ -type rotational transitions are allowed, and  $\Delta K_a = \pm 1$  transitions dominate, while the

pure rotational spectrum only has  $a$ -type transitions ( $\Delta K_a = 0$ ). Hence, the IR data provide a good value for the principal rotational constant  $A$ . Rotational constants and structural parameters for the ground and  $\nu_4 = 1$  states are listed in Tables I and II.

The inertial defect, defined as  $\Delta = I_c - I_a - I_b$ , is identically zero for a planar rigid body. For near-rigid planar molecules,  $\Delta$  is typically a few tenths amu Å<sup>2</sup>, due to a combination of vibrational averaging and Coriolis effects. However,  $\Delta$  values for the ground and  $\nu_4 = 1$  CO<sub>2</sub>-Ar states were found to be 2.44 and 2.39 amu Å<sup>2</sup>, respectively.<sup>8</sup> These large defects are not surprising for floppy complexes. The slight red shift (0.470 cm<sup>-1</sup>) of the band origin for the complexed vs uncomplexed CO<sub>2</sub> asymmetric stretch frequency confirms the weakness of the intermolecular interaction.

Subsequently, Fraser *et al.* used optothermal IR spectroscopy to probe the  $(2\nu_2^0 + \nu_3)/(v_1 + v_3)$  Fermi diad (3612 and 3714 cm<sup>-1</sup>) associated with CO<sub>2</sub> (see Fig. 1).<sup>3</sup> Ground-state rotational constants were in good agreement with those of previous workers,<sup>6,8,9</sup> and using an analysis similar to that of Klemperer and co-workers,<sup>6</sup> they calculated  $\omega_s = 37.5$  and  $\omega_b = 29.4$  cm<sup>-1</sup>.<sup>3</sup> Furthermore, these authors made predictions about the bending potential and intermolecular dynamics based on a Hamiltonian originally developed for describing scattering phenomena,<sup>10</sup> which treats the complex as a rigid stick loosely bound to a ball. In essence, the barrier height for the intermolecular bending coordinate and the center-of-mass separation for the ball and stick are adjusted; rotational and vibrational properties are obtained by diagonalization of the Hamiltonian matrix; and comparison is made between the experimental and model values for the inertial defect and  $\omega_b$ . From such simulations, Fraser *et al.* estimated barrier heights of 200–300 cm<sup>-1</sup> and

TABLE II. Molecular constants for CO<sub>2</sub>-Ar vibrational levels.

	Steed <i>et al.</i> (Ref. 6)	Randall <i>et al.</i> (Ref. 8)	Fraser <i>et al.</i> <sup>3</sup> (Ref. 3)	Present study
Vib. level	Ground	Ground	Ground	Ground <sup>a</sup>
$A$ (MHz)	11 914.(80)	11 904.36(91)	11 953.3(92)	...
$B$	1 929.87(25)	1 978.979(97)	1 979.943(50)	...
$C$	1 682.75(70)	1 683.12(11)	1 682.237(52)	...
$\Delta_J$ (kHz)	18.7	16.97(15)	18.554(38)	...
$\Delta_{JK}$	415.28	360.(11)	360.43(12)	...
$\Delta_K$	-430.	0	0	...
$\delta_J$	2.94	-1.17(41)	2.788(30)	...
$\delta_K$	255.97	-0.94(18)	244.1(41)	...
$\Delta$ (amu Å <sup>2</sup> )	2.65	2.44	2.89	...
Vib. Level	...	$\nu_4 = 1$	$\nu_2 = 2, \nu_4 = 1^c$	$\nu_4 = 1, \nu_5 = 1$
$A$ (MHz)	...	11 814.87(73)	11 850.39(18)	11 833.41(38)
$B$	...	1 977.905(98)	1 978.239(72)	1 976.45(55)
$C$	...	1 680.79(10)	1 680.20(13)	1 680.53(23)
$\Delta_J$ (kHz)	...	16.97(15) <sup>b</sup>	18.554(38) <sup>b</sup>	18.554(38) <sup>b</sup>
$\Delta_{JK}$	...	360.(11) <sup>b</sup>	360.43(12) <sup>b</sup>	360.43(12) <sup>b</sup>
$\Delta$ (amu Å <sup>2</sup> )	...	2.39	2.67	2.32
$\nu_0$ (cm <sup>-1</sup> )	...	2 348.673 152(79)	3611.747 58(4)	3713.835 95 <sup>6</sup>

<sup>a</sup> The ground state constants from Ref. 8 were used in our least-squares fit.

<sup>b</sup> Fixed to ground state value for least-squares fit.

<sup>c</sup> These Fermi diads correspond to the  $(2\nu_2^0 + \nu_3)/(v_1 + v_3)$  diad of uncomplexed CO<sub>2</sub>.

intermolecular stretching and bending frequencies of 22.9 to 28.2 cm<sup>-1</sup>, respectively.<sup>3</sup>

Ideally, one would like to directly measure intermolecular properties. Using IR absorption spectroscopy, we have observed the  $\nu_5$  intermolecular bend in combination with the  $\nu_4$  CO<sub>2</sub> asymmetric stretch. This 4<sub>0</sub><sup>1</sup>5<sub>0</sub><sup>1</sup> combination band is 27.82 cm<sup>-1</sup> higher in energy than the 4<sub>0</sub><sup>1</sup> fundamental, in good agreement with some predictions. In addition, we would like to see if large inertial defects can be accounted for by using semirigid molecular structure theories, as developed by Herschbach and Laurie,<sup>11</sup> and Oka and Morino.<sup>12</sup>

## II. EXPERIMENTAL

Diode lasers have been used extensively in our laboratory to probe vibrationally excited states of weakly bonded complexes, with a "fast-scan" technique exploiting the rapid-tuning capabilities of diode lasers.<sup>13</sup> The apparatus and strategy have been described previously,<sup>14</sup> so only a brief summary is given here.

Dry N<sub>2</sub> is used to purge the entire optical assembly up to the vacuum chamber, and eliminates most atmospheric CO<sub>2</sub> absorption. Tunable IR radiation is obtained by adjusting the current to the diode laser, which is cooled by a closed-cycle He compressor. A single laser mode is selected by dispersing the laser output through a low-resolution monochromator. Power outputs are typically < 0.1 mW per mode. After exiting the monochromator, portions of the radiation are sent to a CO<sub>2</sub> reference cell and an étalon for absolute and relative frequency calibration, respectively. About 90% of the radiation enters the vacuum chamber and is multipassed through the effluent of a pulsed supersonic slit source (38 × 0.15 mm<sup>2</sup>). Nearly parallel, front-surface mirrors define a 13-pass path, resulting in a total absorption length of ~42 cm through the expanding effluent. A recent modification places heaters behind each mirror: keeping these optics at a temperature of ~85 °C prevents diffusion pump oil from condensing on the surfaces. Transmitted intensities from the reference cell, étalon, and effluent were each detected using LN<sub>2</sub>-cooled InSb detector/preamp systems. These signals were acquired simultaneously using three independent digitizers (500 ns × 4000 samples = 2 ms), and signal averaged with a microprocessor.

The fast-scan method transforms absorption signals into a high-frequency regime and operates in the following fashion: (1) Acoustic noise from the cooling compressor triggers a master clock at ~3 Hz. (2) After a set delay, and during a "quiet" period, the pulsed nozzle is opened. (3) Once a stable expansion has formed, the laser frequency is scanned using a linear, adjustable-slope current waveform. Effluent pulse widths are typically > 2 ms. With a tuning rate of 0.25 cm<sup>-1</sup> ms<sup>-1</sup> and absorption linewidths of ~25 MHz, absorption signals will typically have rise times of ~3.3 μs. This transformation successfully avoids the large amplitude, low frequency noise characteristic of mechanically cooled diode lasers. In addition, it circumvents long-term drift in both the laser and étalon. A typical spectrum, covering 0.5 cm<sup>-1</sup> requires 100 averages and takes approximately half a minute.

Samples were prepared prior to expansion by mixing ultrahigh purity (UHP) (99.9995%) CO<sub>2</sub> and UHP Ar in the ratio 1/200. Optimum signals were obtained with a backing pressure ~500 Torr.

## III. RESULTS

While previous IR spectra of CO<sub>2</sub>-Ar had *b*-type selection rules ( $\Delta K_a = \pm 1$ ),<sup>3,8,9</sup> we find only *a*-type ( $\Delta K_a = 0$ ) transitions. Thus, the upper and ground state vibrational wave functions have the same symmetry (i.e., *A*<sub>1</sub>), and we assign the upper state as the  $\nu_4 + \nu_5$  combination (i.e.,  $\nu_4 = 1, \nu_5 = \nu_b = 1$ ). Referring to the normal mode diagram in Fig. 1, it is seen that both  $\nu_4$  and  $\nu_5$  are of *B*<sub>1</sub> symmetry and  $B_1 \otimes B_1 = A_1$ . Furthermore, Bose-Einstein statistics applied to the interchange of the two identical oxygens in CO<sub>2</sub>-Ar allow only totally symmetric wave functions (i.e.,  $K_a = 0, 2, 4, \dots$ ), so even  $\leftarrow$ even  $K_a$  transitions are expected. The  $\nu_4 + \nu_5$  combination band has *B*<sub>1</sub> symmetry and would result in *b*-type transitions.

The  ${}^Q P_0, {}^Q P_2, {}^Q Q_2, {}^Q R_0,$  and  ${}^Q R_2$  bands were observed and used in our rovibrational analysis. A representative spectrum of the  ${}^Q R_0$  and  ${}^Q R_2$  branches appears in Fig. 2 along with a simulated spectrum. Data were fit to a Watson semirigid asymmetric rotor Hamiltonian in the prolate representation:<sup>15</sup>

$$H = \frac{1}{2}(B + C)J^2 + [A - \frac{1}{2}(B + C)]J_a^2 + \frac{1}{2}(B - C)(J_b^2 - J_c^2) - \Delta_J J^4 - \Delta_{JK} J_a^2 J^2 - \Delta_K J_a^4 - 2\delta_J J^2 (J_b^2 - J_c^2) - \delta_K [J_a^2 (J_b^2 - J_c^2) + (J_b^2 - J_c^2) J_a^2]. \quad (1)$$

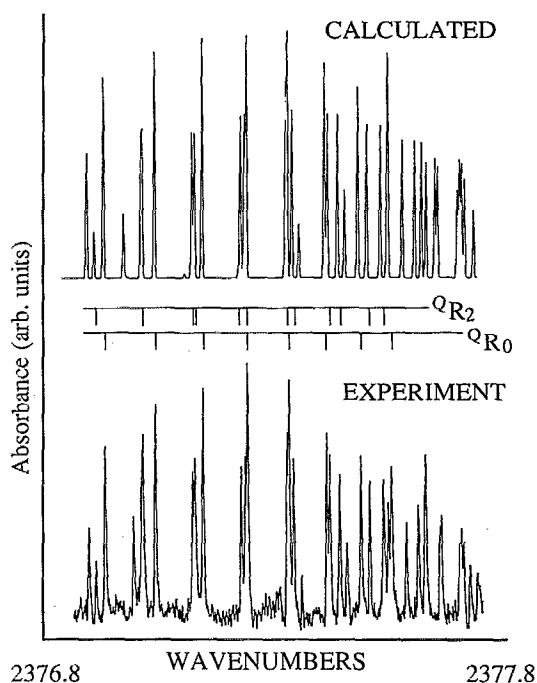


FIG. 2. Representative spectrum of the CO<sub>2</sub>-Ar 4<sub>0</sub><sup>1</sup>5<sub>0</sub><sup>1</sup> combination band. Upper trace is a simulation based on the ground state parameters of Randall *et al.* (see Ref. 8) and the upper state parameters determined here.

Ground-state molecular constants were fixed to the values of randall *et al.*<sup>8</sup> There was little change in the results of our upper-state analysis when the rotational constants of Fraser *et al.*<sup>3</sup> or Sharpe *et al.*<sup>9</sup> were used for the ground state. Combination differences were used to evaluate the upper-state *B* and *C* rotational constants and the quartic distortion constants  $\Delta_J$  and  $\Delta_{JK}$ . All other centrifugal distortion constants were constrained to zero. Although an absolute value for *A* in the upper state could not be obtained from the *a*-type spectrum  $\Delta A$  could be accurately calculated. See Table III for a list of observed line positions and their residuals. An intermolecular bend frequency of 27.8 cm<sup>-1</sup> was estimated by subtracting Randall's *et al.*'s band origin of  $\omega_4 = 2348.67315(8)$  cm<sup>-1</sup> from our combination band origin of 2376.4913(2) cm<sup>-1</sup>. This value (27.8181 cm<sup>-1</sup>) is close to the true bend frequency, differing only by the coupling between  $\nu_4$  and  $\nu_b$ . Comparison of the  $\nu_4 + \nu_b$  rotational constants with those of the ground state shows a small

but significant change in *A*, *B*, and *C* (~5%). Specifically, *A* increases by 544 MHz, while *B* and *C* decrease by 70 and 77 MHz, respectively.

Several simple equations have been used that relate observed spectroscopic constants to structural parameters:

$$R = [I_c - I_{\text{CO}_2}] / \mu^{1/2} = [(G/\mu)(C^{-1} - B_{\text{CO}_2}^{-1})]^{1/2}, \quad (2)$$

$$\sin \theta = \sqrt{\frac{(I_a - I_c)I_a}{(I_{\text{CO}_2} - I_c)I_{\text{CO}_2}}} + \frac{b}{A} \sqrt{\frac{C - A}{C - B_{\text{CO}_2}}}, \quad (3)$$

where  $I_a$  and  $I_c$  are moments of inertia of the complex (amu  $\text{\AA}^2$ ) with *A* and *C* the corresponding rotational constants,  $\mu$  is the reduced mass between CO<sub>2</sub> and Ar,  $I_{\text{CO}_2}$  and  $B_{\text{CO}_2}$  are the moment of inertia and rotational constant of uncomplexed CO<sub>2</sub>, and *G* is a proportionality constant (16.857 52 amu  $\text{\AA}^2/\text{cm}^{-1}$ ) which accounts for unit conver-

TABLE III. Transitions and residuals ( $\nu_{\text{obs}} - \nu_{\text{calc}}$ ) for the 4<sub>0</sub><sup>1</sup>5<sub>0</sub><sup>1</sup> CO<sub>2</sub>-Ar combination band; units in cm<sup>-1</sup>,  $\sigma_{\text{rms}} = 0.0005$  cm<sup>-1</sup>.

Transition	Observed	Residual	Transition	Observed	Residual
2 <sub>2,1</sub> -3 <sub>2,2</sub>	2376.1796	-0.0003	5 <sub>2,3</sub> -5 <sub>2,4</sub>	2376.4898	0.0004
2 <sub>2,0</sub> -3 <sub>2,1</sub>	2376.1796	0.0005	5 <sub>2,4</sub> -5 <sub>2,3</sub>	2376.4744	0.0003
3 <sub>2,2</sub> -4 <sub>2,3</sub>	2376.0412	-0.0008	6 <sub>2,4</sub> -6 <sub>2,5</sub>	2376.4646	-0.0002
3 <sub>2,1</sub> -4 <sub>2,2</sub>	2376.0412	0.0013	6 <sub>2,5</sub> -6 <sub>2,4</sub>	2376.4349	0.0005
4 <sub>2,3</sub> -5 <sub>2,4</sub>	2375.8987	-0.0003	7 <sub>2,5</sub> -7 <sub>2,6</sub>	2376.4387	-0.0006
4 <sub>2,2</sub> -5 <sub>2,3</sub>	2375.8946	-0.0001			
5 <sub>2,4</sub> -6 <sub>2,5</sub>	2375.7504	-0.0004	1 <sub>0,1</sub> -0 <sub>0,0</sub>	2376.6088	0.0004
5 <sub>2,3</sub> -6 <sub>2,4</sub>	2375.7428	-0.0006	2 <sub>0,2</sub> -1 <sub>0,1</sub>	2376.7202	0.0000
6 <sub>2,5</sub> -7 <sub>2,6</sub>	2375.5972	-0.0004	3 <sub>0,3</sub> -2 <sub>0,2</sub>	2376.8262	-0.0003
6 <sub>2,4</sub> -7 <sub>2,5</sub>	2375.5857	-0.0002	4 <sub>0,4</sub> -3 <sub>0,3</sub>	2376.9273	0.0002
7 <sub>2,6</sub> -8 <sub>2,7</sub>	2375.4389	-0.0004	5 <sub>0,5</sub> -4 <sub>0,4</sub>	2377.0217	0.0001
7 <sub>2,5</sub> -8 <sub>2,6</sub>	2375.4221	-0.0001	6 <sub>0,6</sub> -5 <sub>0,5</sub>	2377.1103	0.0004
8 <sub>2,7</sub> -9 <sub>2,8</sub>	2375.2758	-0.0002	7 <sub>0,7</sub> -6 <sub>0,6</sub>	2377.1922	0.0004
8 <sub>2,6</sub> -9 <sub>2,7</sub>	2375.2523	-0.0001	8 <sub>0,8</sub> -7 <sub>0,7</sub>	2377.2676	0.0005
9 <sub>2,8</sub> -10 <sub>2,9</sub>	2375.1077	-0.0001	9 <sub>0,9</sub> -8 <sub>0,8</sub>	2377.3362	0.0004
9 <sub>2,7</sub> -10 <sub>2,8</sub>	2375.0756	-0.0011	10 <sub>0,10</sub> -9 <sub>0,9</sub>	2377.3984	0.0006
10 <sub>2,9</sub> -11 <sub>2,10</sub>	2374.9345	-0.0001	11 <sub>0,11</sub> -10 <sub>0,10</sub>	2377.4533	0.0001
10 <sub>2,8</sub> -11 <sub>2,9</sub>	2374.8956	0.0002	12 <sub>0,12</sub> -11 <sub>0,11</sub>	2377.5017	-0.0004
1 <sub>0,1</sub> -2 <sub>0,2</sub>	2376.2422	0.0000	3 <sub>2,2</sub> -2 <sub>2,1</sub>	2376.8965	0.0004
2 <sub>0,2</sub> -3 <sub>0,3</sub>	2376.1104	-0.0002	3 <sub>2,1</sub> -2 <sub>2,0</sub>	2376.8965	-0.0004
3 <sub>0,3</sub> -4 <sub>0,4</sub>	2375.9745	-0.0002	4 <sub>2,3</sub> -3 <sub>2,2</sub>	2376.9967	0.0003
4 <sub>0,4</sub> -5 <sub>0,5</sub>	2375.8339	-0.0007	4 <sub>2,2</sub> -3 <sub>2,1</sub>	2376.9983	-0.0003
5 <sub>0,5</sub> -6 <sub>0,6</sub>	2375.6900	-0.0005	5 <sub>2,4</sub> -4 <sub>2,3</sub>	2377.0912	0.0000
6 <sub>0,6</sub> -7 <sub>0,7</sub>	2375.5426	0.0001	5 <sub>2,3</sub> -4 <sub>2,2</sub>	2377.0959	0.0003
7 <sub>0,7</sub> -8 <sub>0,8</sub>	2375.3912	0.0004	6 <sub>2,5</sub> -5 <sub>2,4</sub>	2377.1801	-0.0003
8 <sub>0,8</sub> -9 <sub>0,9</sub>	2375.2352	0.0000	6 <sub>2,4</sub> -5 <sub>2,3</sub>	2377.1880	-0.0001
9 <sub>0,9</sub> -10 <sub>0,10</sub>	2375.0755	-0.0001	7 <sub>2,6</sub> -6 <sub>2,5</sub>	2377.2640	0.0001
10 <sub>0,10</sub> -11 <sub>0,11</sub>	2374.9108	-0.0010	7 <sub>2,5</sub> -6 <sub>2,4</sub>	2377.2761	0.0000
			8 <sub>2,7</sub> -7 <sub>2,6</sub>	2377.3422	0.0006
2 <sub>2,0</sub> -2 <sub>2,1</sub>	2376.5463	0.0000	8 <sub>2,6</sub> -7 <sub>2,5</sub>	2377.3597	-0.0001
2 <sub>2,1</sub> -2 <sub>2,0</sub>	2376.5463	0.0005	9 <sub>2,8</sub> -8 <sub>2,7</sub>	2377.4138	0.0002
3 <sub>2,1</sub> -3 <sub>2,2</sub>	2376.5300	-0.0011	9 <sub>2,7</sub> -8 <sub>2,6</sub>	2377.4390	-0.0002
3 <sub>2,2</sub> -3 <sub>2,1</sub>	2376.5300	0.0011	10 <sub>2,9</sub> -9 <sub>2,8</sub>	2377.4804	0.0008
4 <sub>2,2</sub> -4 <sub>2,3</sub>	2376.5119	0.0001	10 <sub>2,8</sub> -9 <sub>2,7</sub>	2377.5148	0.0007
4 <sub>2,3</sub> -4 <sub>2,2</sub>	2376.5055	0.0002			

sions.<sup>8</sup> Values of 43.2004 and 43.5439 amu Å<sup>2</sup> were used for the ground and excited state moments of inertia of CO<sub>2</sub>, respectively. When applied to the effective molecular constants corresponding to the upper state, we find  $\langle \theta \rangle = 77.7^\circ$  and  $\langle R \rangle = 3.60$  Å. These values are contrasted to the geometric parameters of the ground and  $v_4 = 1$  states in the top half of Table I. Note the increase in  $\langle R \rangle$  of 3% and decrease in  $\langle \theta \rangle$  of 7%–8% relative to the ground and  $v_4 = 1$  states.

Despite extensive searches for the combination band with the intermolecular stretch (i.e., up to 75 cm<sup>-1</sup> above  $\omega_4$ ), these transitions were not to be found.

#### IV. DISCUSSION

Concern has been expressed regarding the extraction of unique potential surfaces from spectra of floppy systems. Specifically, Nesbitt and Naaman showed that Watson-type Hamiltonians do not necessarily yield moments of inertia that reflect the actual potential surface.<sup>16</sup> They calculated rovibrational eigenstates for an artificially flat triatomic-bender potential using rigorous techniques. The resulting energy eigenvalues were then analyzed with a Watson Hamiltonian and the overall fitting error was found to be within the limits imposed by a typical IR experiment. The original potential and the one inferred by the Watson Hamiltonian exhibited major differences.

Despite the pitfalls, we wished to see if the standard theory of semirigid molecules could account for the large observed inertial defects. The procedure, first introduced by Herschbach and Laurie,<sup>11</sup> and Oka and Morino,<sup>12</sup> involves attributing the effective moments of inertia to three contributions:

$$I^{\text{eff}} = I^0 + \delta I_{\text{har}} + \delta I_{\text{cor}}. \quad (4)$$

The  $I^0$  term, called the standard moment of inertia, corresponds to some reference geometry that is close enough to the equilibrium geometry to justify the retention of only the leading terms in power series expansions.<sup>11</sup> The  $\delta I_{\text{har}}$  term arises from averaging over vibrational amplitudes. For planar molecules, the individual  $\delta I_{\text{har}}$  are affected by both in-plane and out-of-plane vibrations, but only the latter have an effect on the inertial defect. The  $\delta I_{\text{cor}}$  term takes into account Coriolis effects. This is often the most important term in planar systems, and is neglected in conventional Watson Hamiltonians. Although Eq. (4) should contain both harmonic and anharmonic contributions, we have considered only the former in our analysis: it has been shown that the anharmonic contributions cancel in calculating the inertial defect for planar molecules. In so doing, the derived standard configuration corresponds to the *average* structure rather than the *equilibrium* structure. The full treatment of Herschbach and Laurie takes into account anharmonicity, but requires knowledge of the additional parameters.<sup>11</sup> Equation (4) can be written as a sum over vibrational modes:

$$I_{\alpha\beta}^{\text{eff}} = \delta_{\alpha\beta} I_{\alpha}^0 + \sum_n (v_n + d_n/2) \epsilon_n^{\alpha\beta}, \quad (5)$$

where  $\delta_{\alpha\beta}$  is the Kronecker delta and  $d_n$  is the degeneracy of

the  $n$ th mode. Notice that  $\delta I_{\text{har}}$  and  $\delta I_{\text{cor}}$  are contained within  $\epsilon_n^{\alpha\beta}$ , the perturbation elements to the inertial tensor. As derived by Oka *et al.*, the perturbation elements to the inertial tensor may be conveniently expressed as<sup>12</sup>

$$\epsilon_n^{\alpha\beta} = \left( \frac{-6G}{\omega_n} \right) \left( A_{nn}^{\alpha\beta} - \frac{4}{3} \sum_m \zeta_{nm}^{\alpha} \zeta_{nm}^{\beta} \frac{\omega_m^2}{\omega_m^2 - \omega_n^2} \right), \quad (6)$$

where  $G$  is the proportionality constant defined earlier and  $\omega_n$  is the frequency of the  $n$ th normal mode. The first term,  $A_{nn}^{\alpha\beta}$ , corresponds to vibrational averaging contributions and is defined as  $\langle \partial^2 I_{\alpha\beta} / \partial Q_n^2 \rangle$  from the Taylor expansion of  $I_{\alpha\beta}$  in terms of normal mode coordinates  $Q_n$ . The second term is the Coriolis interaction, with  $\zeta_{nm}^{\alpha}$  the coupling constant between the  $n$ th and  $m$ th modes undergoing rotation about the  $\alpha$  principal rotational axis. For  $\zeta_{nm}^{\alpha}$  to be nonzero,  $Q_n \otimes Q_m$  must contain the symmetry representation corresponding to one of the principal  $P_{\alpha}$  (projection of rotational angular momentum). Both  $A_{nn}^{\alpha\beta}$  and  $\zeta_{nm}^{\alpha}$  have simple analytical expressions:<sup>11</sup>

$$A_{nn}^{\alpha\alpha} = \sum_i m_i [(\delta\beta_{in})^2 + (\delta\gamma_{in})^2], \quad (7)$$

$$A_{nn}^{\alpha\beta} = - \sum_i m_i (\delta\beta_{in} \delta\alpha_{in}), \quad (8)$$

$$\zeta_{nm}^{\alpha} = \sum_i m_i (\delta\beta_{in} \delta\gamma_{im} - \delta\gamma_{in} \delta\beta_{im}), \quad (9)$$

where  $\delta\alpha_{ij}$ ,  $\delta\beta_{ij}$ , and  $\delta\gamma_{ij}$  are orthogonal displacement coordinates for the  $i$ th atom undergoing vibration in the  $n$ th normal mode. The Cartesian displacement vectors are calculated from the transformation coefficients which are, in turn, obtained by solving the Wilson secular equation:  $\det|\mathbf{FG} - E\lambda| = 0$ .

The approach used to model CO<sub>2</sub>-Ar inertial defects is as follows. A  $G$  matrix was constructed by assuming a  $C_{2v}$  equilibrium geometry and by using CO<sub>2</sub> monomer equilibrium values and the value of  $R_{\text{cm}}$  determined above. Where available, experimentally measured frequencies were used to construct the  $F$  matrix. Upon solving the secular equation, Cartesian displacement vectors were generated for each normal mode, and Eqs. (5)–(9) were used to calculate the perturbation terms to the inertial tensor. Several different CO<sub>2</sub>-Ar distances were tried, but moderate changes (i.e., ~5%) had little effect on the perturbation terms. Inertial defects were then calculated for all vibrational modes, as summarized in Table IV. It is interesting to note that ground state inertial defects arising from  $v_2$  and  $v_6$  are of equal magnitude but opposite sign, and almost cancel. These two vibrations correspond to the in-plane and out-of-plane CO<sub>2</sub> bend, respectively. As expected, almost all of the inertial defect arises from the intermolecular bend,  $v_3$ . Inertial defects were also calculated for vibrationally excited CO<sub>2</sub>-Ar (both  $v_4$  and  $v_4 + v_b$ ) and compared to experimental values; agreement is good.

#### V. CONCLUSION

Large-amplitude and Coriolis contributions are seen to account for most of the inertial defect, as shown in the bottom half of Table I. However, this result was obtained by

TABLE IV. Contribution per quantum of each normal mode (see Fig. 1) to the inertial defect (units of amu Å<sup>2</sup>).

Mode	$\nu_1$	$\nu_2$	$\nu_3$	$\nu_4$	$\nu_5$	$\nu_6$
Frequency (cm <sup>-1</sup> )	1330.0 <sup>a</sup>	679.0 <sup>a</sup>	36.0 <sup>b</sup>	2347.0 <sup>c</sup>	27.8 <sup>c</sup>	673.0 <sup>a</sup>
$\Delta$ (Harmonic)	0.00	0.00	0.00	0.00	0.00	0.30
$\Delta$ (Coriolis)	0.00	6.04	-0.43	0.00	5.41	-6.30
$\Delta$ (Harmonic + Coriolis)	0.00	6.04	-0.43	0.00	5.41	-6.00

<sup>a</sup> Monomer force constants used.

<sup>b</sup> From centrifugal distortion; see Ref. 6.

<sup>c</sup> Measured; see main text.

summing the entries from Table IV, and one sees that the *net* inertial defect is the sum of both *positive* and *negative* contributions from the six vibrational modes, four of which give nonzero entries. This cancellation of positive and negative terms indicates that the result is sensitive to the intermolecular potential, which is not known, and approximated crudely by harmonic force fields. Thus, the agreement between the calculated and observed inertial defects should not be taken as supporting the model until a better intermolecular force field is used; the present agreement could be quite fortuitous.

The  $R$  and  $\theta$  values listed in Table I correspond to average values, since we have included only harmonic terms in the potentials. These values seem reasonable, but we presently have no means of independent verification. In fact, since the harmonic corrections do not account for the variations in the  $R$  and  $\theta$  values between vibrational states, we may conclude that the anharmonic contributions are the most important. With a better force field (e.g., from *ab initio* or electrostatic calculations) it may be possible to add sufficient anharmonicity to test convergence toward the equilibrium structure, while accounting for nearly all of the inertial defect.

In summary, we have observed the intermolecular bend in combination with the  $\nu_4$  CO<sub>2</sub> asymmetric stretch of gaseous CO<sub>2</sub>-Ar complexes, using IR absorption spectroscopy. This combination band is  $\sim 10^2$  times less intense and 27.8 cm<sup>-1</sup> higher in energy than the  $\nu_4$  fundamental. Analyses based on a Watson Hamiltonian using the observed moments-of-inertia yield  $\langle \theta \rangle = 78^\circ$  and  $\langle R \rangle = 3.6$  Å for the  $\nu_4 + \nu_b$  vibrationally excited state, compared to 83° and 3.5 Å for the ground state. Large inertial defects were observed in the ground and excited states,  $\Delta = 2.44$  and 9.48 amu Å<sup>2</sup>, respectively. Most of these defects are accounted for by using a simple model in which vibrational averaging and Coriolis effects are calculated explicitly. However, agreement is al-

most "too good," given the rough nature of the model, and further comparisons will be needed to test the viability of the model<sup>11,12</sup> with weakly bonded complexes.

## ACKNOWLEDGMENTS

We thank Y. Y. Bai and Y. P. Zeng for many useful discussions. Particular thanks go to R. B. Gerber, who prompted us to search for the combination band. Research supported by the U.S. Army Research Office under the auspices of the Center for the Study of Fast Transient Processes.

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