13348 J. Phys. Chem. 1993, 97, 13348–13354

Ultraviolet and Polarized Infrared Spectroscopy of Matrix-Isolated Cyclobutadiene and Its Isotopomers

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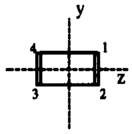
Received: June 1, 1993[●]

The UV and polarized IR spectra of argon matrix isolated cyclobutadiene and its *1-d-*, *1,2-*d_2-, *1,4-*d_2-, *1-*^{13}C-, *1,2-*$^{13}C_2$-, and *1,4-*$^{13}C_2$-labeled derivatives are reported. Above 250 nm, the UV spectrum contains no peaks with an extinction coefficient larger than 10 L M^{-1} cm^{-1}, but a weak absorption tail extends throughout the UV region. The absorption rises abruptly below 250 nm. The IR peak positions mostly agree with previous reports where these are available. Photoalignment studies support the symmetry assignment of fundamental vibrations and prove that the two Kekulé forms interconvert rapidly even at 10 K. The spectral and photochemical effects of the presence of an adjacent CO_2 molecule in the cyclobutadiene matrix site are elucidated. Its presence causes a substantial retardation of the photofragmentation of cyclobutadiene into two acetylenes. This is attributed to accelerated vibrational energy loss from the cyclobutadiene absorber.

Few molecules have sustained the interest of experimental and theoretical chemists as has cyclobutadiene (**1**). Since it was first postulated,[2] reports of the properties of this molecule have been shrouded in controversy, which has yet to be fully resolved.[3,4] There have been numerous spectroscopic studies that have revealed much about its properties,[3–10] although it was only observed at low temperature in glasses or inert gas matrices until recently.[11–13]



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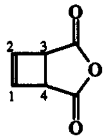

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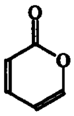

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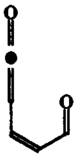

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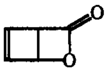

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In spite of this considerable effort, too few of the fundamental vibrations of **1** and its isotopomers are known presently to establish its force field. Its UV–visible spectrum has yet to be unambiguously identified,[4,6–10] let alone assigned. The rate of valence tautomerism, a process that is believed to occur mainly through heavy atom tunneling,[14–19] has yet to be measured.

Matrix effects have complicated the assignments of both the IR and UV spectra. In particular, side products, produced along with **1** and trapped within the same matrix cavity, have interfered with the identification of fundamental vibrations. The nature of the interactions between **1** and these companion molecules is unknown.

We now report UV and IR spectra of **1** and its isotopically labeled derivatives, permitting us to settle some of these disputes. Polarized IR spectroscopy on samples partially oriented by photoselection has allowed an unambiguous symmetry assignment of the observed vibrations as in-plane or out-of-plane polarized and contributed to the identification of others. This approach has also confirmed the occurrence of rapid interconversion between the two valence tautomeric rectangular forms in low-temperature matrix environment and has yielded information concerning many of the puzzling aspects of the cyclobutadiene–matrix partner interactions.

A brief communication of some of the present results has appeared.[18]

Experimental Section

The anhydride precursor (**2**) was synthesized using a modified version of a previously reported synthetic method.[20,21] A low-temperature Pyrex immersion photolysis vessel (Ace Glass 7841 and 7858), with a magnetic stirring bar in the bottom, was filled with ethyl acetate (290 mL), maleic anhydride (5 g), and acetophenone (1.0 mL). The three inlet ports were sealed with two glass stoppers and one rubber septum. A rubber bladder (Harvis Novelty) was filled with 2–3 L of welder's grade acetylene. The neck of the bladder was then fitted over the barrel of a hypodermic syringe. The syringe, in turn, was fitted with a 25-cm-long small-bore needle that could be forced through the septum to the bottom of the photolysis vessel. The photolysis vessel was cooled to −78 °C in a dry ice–acetone bath. Acetylene is very soluble in ethyl acetate at these temperatures, and after approximately 1 h the bladder was almost empty. The Hg lamp (Hanover 450 W) was then ignited and the progress of the reaction monitored by GC (6 ft, 5% SE 30, 100–200 °C min^{-1}) until the maleic anhydride was consumed. The reaction vessel was allowed to warm to room temperature while precipitation of maleic anhydride dimer occurred. After filtration, short-path distillation under reduced pressure (10 mTorr, the fraction above 75 °C being mostly the desired product), and recrystallization from anhydrous ether, 2.8 g of colorless needles were collected (56% yield, mp 84–85 °C).

The labeled precursors were produced by similar methods except that labeled acetylenes were used in the photochemical 2+2 addition. Acetylene-d_1 was produced by the method of Lompa-Krzymien and Leitch.[22] Acetylene-d_2 was produced by the addition of D_2O to CaC_2 and bulb-to-bulb distilled. Acetylene-$^{13}C_1$ was purchased from MSD isotopes and used as received. Labeled barium carbide, produced by reacting Mg dust (5 g) with $Ba^{13}CO_3$ (1 g) under vacuum (~800 °C) was used to synthesize the $^{13}C_2$-labeled acetylene. In all cases infrared, ^1H and ^{13}C NMR spectra, as well as melting points and mass spectra were consistent with the anhydride structure. The isotopic purity, by mass spectroscopy, for all samples was >95%, except for the d_1-labeled sample, which was ca. 80% (15% d_2 and 5% unlabeled).

The matrix isolation experiments used argon or neon (both from Matheson, 99.999% purity). The matrix gas was deposited on a polished CsI or sapphire deposition window, depending on whether IR or UV spectra were to be obtained. For argon matrices, the deposition window was mounted on the second stage of a closed-cycle refrigerator (Air Products Displex 202) by an oxygen-free copper sample holder which was maintained at 30

[●] Abstract published in *Advance ACS Abstracts*, November 1, 1993.

0022-3654/93/2097-13348$04.00/0

K during the deposition. The sample was produced by codeposition of a stream of argon and a stream of vapor of **2**, generated by room-temperature sublimation, onto the deposition window. In general, gas flow rates of 0.01 mol of matrix gas/h were used to produce matrices with matrix ratios between 1:5000 and 1:10 000. Irradiation of inert gas matrices was carried out using either a Lambda-Physik EMG-50 excimer laser (248 or 308 nm) or a Mineralight UVGL25 mercury lamp with the filter removed to allow both the long and short wavelengths to impinge upon the sample.

Neon matrices were produced in a similar fashion, but the cryostat was replaced by an Air Products Heliplex closed-cycle refrigerator (APD Cryogenics HC-4 MK1, Heliplex Assembly HS-4). For the deposition of neon the Heliplex cold-stage temperature was maintained at 4 K.

Partially oriented solid solutions were obtained using the method of photoselection. Emission from a Lambda Physik EMG-50 excimer laser operating at 248 nm was passed through a Wollaston polarizer to obtain linearly polarized light with an electric vector defining the laboratory *Z* axis.

IR spectra were measured with a Nicolet 60 SXR FTIR spectrometer at 1-cm^{-1} resolution and a Cambridge Physical Sciences 1GP-225 polarizer. Dichroism was evaluated in three ways, all of which gave identical results: comparison of peak heights, peak areas, and spectral subtraction. UV spectra were recorded with a Cary 2300 spectrometer and Glan-Thompson polarizers.

Results and Discussion

Photochemical Generation of 1. We have chosen the anhydride **2** as a photochemical precursor for matrix-isolated **1**. Although the usefulness of **2** has been demonstrated,[8,9] it is not a clean source of **1**, and our initial efforts were directed at the removal of the contributions of byproducts to the UV and IR spectra. Close inspection of the UV-visible and infrared spectra obtained by monochromatic 248-nm radiation revealed that the photochemistry of **2** is complicated by reactions that lead to α-pyrone **3** and the aldoketene **4**, as well as the lactone **5**. The photochemical interconversions of **3**–**5** have been well studied,[23] as has the 1–5 hydrogen shift in the aldoketone **4** that causes a scrambling of isotopic labels in **3**.[24] Since **5** is a known[5,6] precursor to **1**, it is not clear *a priori* what percentage of the observed **1** is produced directly from **2** and how much is produced indirectly through the intermediate **5**.

The appearance of **5** in the matrix can be attributed to the loss of CO from **2** followed by ring closure of the expected biradical intermediate. Starting with **2** labeled in positions 1 and 2 and assuming that the "biradical" has a significant lifetime there may be a scrambling of the labels to produce a mixture of 1,2- and 1,4-labeled **5**. An opening of **5** to **4**, possibly via **3**, followed by the known 1,5 hydrogen atom shift will cause changes in the connectivity of deuterium atoms and will open the possibility of loss of a ^{13}C label as a $^{13}CO_2$ fragment. We do not observe changes in the connectivity of the deuterium atoms in the case of **2** labeled with deuterium in positions 1 and 2, nor is enriched $^{13}CO_2$ observed in the case of 1,2-^{13}C labeled **2**. There are two possible explanations for this observation. Either very little of the observed **1** is produced through the intermediate **5**, or the loss of CO from **2** results in only one of the two possible isomers of labeled **5**. Our experiments cannot differentiate between the two possibilities although it seems reasonable to assume that the production of **5** is a minor pathway in the photochemistry of **2** and that most of the observed **1** is produced directly from **2**.

UV-Visible Absorption. The literature on the electronic absorption spectrum of **1** is very confusing. It has been reported, in matrix or glass isolation, that unsubstituted **1** exhibits a broad absorption peak near 300–305 nm with ϵ_{max} roughly estimated at 100.[4b,7] It has been proposed[9] and disputed[4b] that this peak is to be attributed not to free **1** but to its complex with CO_2. A report[6] of a different broad and weak absorption band at 405 nm was later disproved.[10] We find that after the irradiation of **2** at 248 nm and subsequent bleaching with 254- and 313-nm light to destroy **3**–**5**, the matrix contains CO, CO_2, acetylene, and appreciable quantities of **1** as evidenced by its IR spectrum (vide infra). UV-visible and infrared spectra obtained on the same sample, deposited on a sapphire deposition window, show no observable UV-visible band maximum above 230 nm, even though bands known to belong to **1** are observable in the infrared (Figure 1). Sapphire absorbs below 2000 cm^{-1} so that only the C–H stretching region could be obtained. As will be shown below, the "complex" of **1** with CO_2 is not easily destroyed by these wavelengths so that it cannot have an absorption maximum at wavelengths greater than 230 nm either.

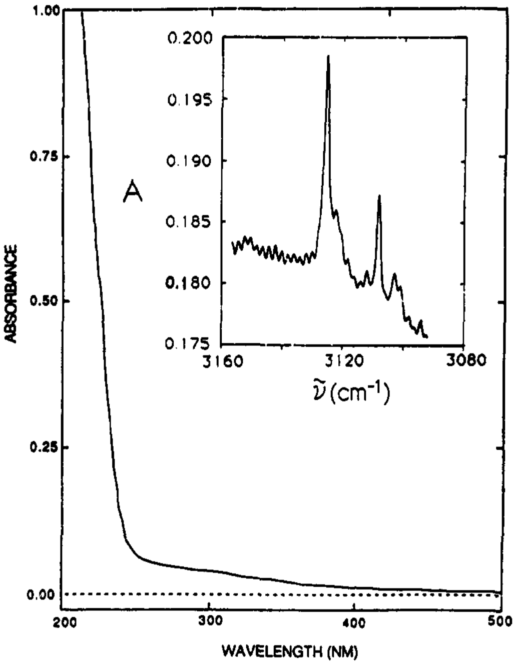

Figure 1. UV and FTIR (inset) spectra of argon-matrix isolated **1** on a sapphire deposition window.

It is possible to estimate the maximum absorptivity that a transition in the 250–400-nm region could have and yet remain undetected in these experiments. From the relative ratios of acetylene, before and after complete destruction of **1** with 254-nm light, it is estimated that ~50% of the **1** originally formed had already been destroyed before the UV spectrum in Figure 1 was obtained. The absorbance of the initial sample before irradiation with 248-nm light was 0.56 and the molar extinction coefficient of **2** in a number of solvents at room temperature is known[4a,8] to be $\epsilon = 670$ L M^{-1} cm^{-1}. Assuming an absorbance peak of 0.01 absorbance units could be detected, the highest possible molar extinction coefficient for an absorption maximum of **1** in this region is $\epsilon \sim 10$ L $M^{-1}cm^{-1}$. Below 250 nm, **1** absorbs more strongly but the location of the band maximum is not known.

However, **1** must have a weak absorption tail extending to at least 420 nm, and faintly apparent in Figure 1, since continued irradiation of matrix-isolated **1** with light from a Xe lamp, filtered to allow only 350–420-nm light to strike the sample, slowly bleaches the IR signals of **1** and increases those of acetylene.

IR Absorption. The best infrared spectrum of **1** has been obtained as a subtraction of spectra obtained before and after 36 h of 350–420-nm irradiation of a sample of matrix-isolated **1**. In Figure 2, bands due to **1** have positive absorbance, those of the photoproducts of cyclobutadiene decomposition have negative absorbance. The large bands that appear both positive and negative are due to CO and CO_2. Their appearance is due to radiation-induced changes in the matrix site in which these

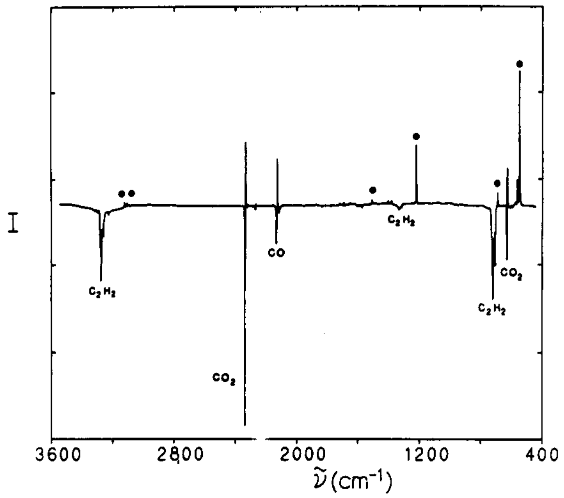

Figure 2. FTIR spectrum of matrix-isolated **1**. The spectrum was obtained as a difference of the spectra before and after photodestruction of **1** with 350–420-nm light. The photoproducts are shown with negative intensity.

molecules reside. The frequencies of these vibrations are sensitive to the matrix partner, be it **1** or acetylene, as will be shown below. Besides the known fundamentals of **1** at 576, 721, 1245, and 1526 cm^{-1}, two bands at 3124 and 3107 cm^{-1} are clearly observed.[18] These are assigned as the b_{1u} C–H stretch and the b_{2u} C–H stretch, respectively, on the basis of the calculated frequencies and intensities.[25] These two stretches were also assigned at 3073 and 3105 cm^{-1} when a tricyclic precursor was used.[4a] While the 3107- and 3105-cm^{-1} assignments appear identical, we have no explanation for the discrepancy between this report and our observation of the other stretch at 3124 cm^{-1}.

All of these fundamentals appear with the same relative intensity in all of the spectra and are produced and decomposed at the same rate. There have been reports of the seventh and last missing IR-active fundamental and of several overtone vibrations,[4a] but the reported bands do not appear in the spectrum shown in Figure 2. We therefore conclude that these bands do not belong to **1** and do not list them in Table I.

IR Spectra of Isotopomers. Four isotopically labeled precursors (**2**-*1*-*d*, **2**-*1*,*2*-d_2, **2**-*1*-^{13}C, **2**-*1*,*2*-$^{13}C_2$) were deposited and irradiated using the same procedure as described above. The IR frequencies and assignments are collected in Table I. Notice that for each doubly labeled precursor there are two possible labeled cyclobutadiene products, the 1,4- and the 1,2-labeled species, and both are always observed with equal concentration based on the calculated relative intensities.[25] While this observation is consistent with rapid valence tautomerization, we cannot positively rule out that mixing of the labels has occurred via an alternate mechanism.

With the singly labeled cyclobutadienes of C_s symmetry, each in-plane fundamental is split by 4 cm^{-1}, while the out-of-plane bending modes are split by ~15 cm^{-1}. The smaller splitting is believed to be a matrix effect where the single label on **1** causes a splitting of matrix sites that are degenerate in the case of higher symmetry labeled **1**.

Raman Spectra and the Tunneling Problem. A normal-mode analysis for **1** requires the knowledge of frequencies of the IR-inactive vibrations as well as the IR-active vibrations. We have included in Table I the reported frequencies for the observed Raman active fundamentals of unlabeled **1**.[19] Table I also shows the frequencies calculated for all of the fundamentals of free **1** at the MP2/631G* level of theory.[25] These calculations were later extended to account for the anharmonicity of the totally symmetric vibrational modes[17] and predicted a 4.6-cm^{-1} tunneling splitting for the ground state as well as larger splittings of the a_g fundamentals, and 2.6 × 10^{11} s^{-1} as the tunneling rate. Although the theoretical treatment was still quite crude, it left little doubt that the initial proposal[14] was correct and that quantum mechanical tunneling of carbon atoms must be an important contributor to the valence tautomerization rate of **1**. This conclusion is supported by matrix-isolated ^{13}C NMR measurements[18] on vicinally doubly ^{13}C-labeled **1**, compatible only with a tunneling rate that is fast on the NMR time scale.

TABLE I: Observed IR Vibrational Frequencies of Cyclobutadiene and Its Isotopic Derivatives (cm^{-1})

compd	obsd	K_l[a]	assignment[b]	calcd[c]
1	531[d]		(b_{2g})	500
	576	0.379	b_{3u} opb	572
	721	0.297	b_{2u} rd	721
	723[d]		(b_{3g})	861
	989[d]		(a_g)	992
	1059[d]		(a_g)	1150
	1245	0.298	b_{2u} ipb	1319
	1526	0.290	b_{1u}C═C str	1620
	1678[d]		(a_g)	1604
	3093[d]		(b_{3g})	3265
	3107	0.294	b_{2u} C–H str	3275
	3124	0.292	b_{1u} C–H str	3270
	3140[d]		(a_g)	3309
1-d_1	449		opb	534[f]
	595		opb	625[f]
	633		opb	682[f]
	787 (790)[e]		rd	741[f]
	1224 (1228)[e]		ipb	1372[f]
	1538 (1541)[e]		C═C str	1769[f]
1-*1*,*2*-d_2[g]	445	0.362	b_1 opb	434
	582	0.363	b_1 opb	568
	1213	0.301	b_2 ipb	1275
	1442	0.308	a_1 C═C str	1557
	1509	0.299	a_1 C═C str	1613
	3085	0.30 ± 0.01	b_2 C–H str	3268
	3131	0.30 ± 0.01	a_1 C–H str	3291
1-*1*,*4*-d_2[g]	478	0.363	b_1 opb	475
	634	0.300	a_1 rd	635
	770	0.371	b_1 opb	788
	1190	0.298	a_1 ipb	1259
	1486	0.306	a_1 C═C str	1592
	3085	0.30 ± 0.01	b_2 C–H str	3265
	3131	0.30 ± 0.01	a_1 C–H str	3293
1-$^{13}C_1$	574	0.348	opb	670[f]
	712 (715)[e]	0.325 (0.330)	rd	793[f]
	1237 (1241)[e]	0.328 (0.329)	ipb	1392[f]
	1517 (1521)[e]	0.322 (0.330)	C═C str	1772[f]
	3122	0.32 ± 0.01	C–H str	3365[f]
	3105	0.32 ± 0.01	C–H str	3387[f]
1-*1*,*2*-$^{13}C_2$[g]	549	0.355	b_1 opb	562
	570	0.351	b_1 opb	572
	708	0.320	b_2 rd	711
	1238	0.321	b_2 ipb	1311
	1541	0.315	a_1 C═C str	1555
	1560	0.328	a_1 C═C str	1614
	3045	0.32 ± 0.01	a_1 C–H str	3264
	3051	0.32 ± 0.01	b_1 C–H str	3272
1-*1*,*4*-$^{13}C_2$[g]	570	0.351	b_1 opb	571
	708	0.320	a_1 rd	712
	1238	0.321	a_1 ipb	1310
	1560	0.328	b_2 C═C str	1592
	3042	0.32 ± 0.01	b_2 C–H str	3267
	3049	0.32 ± 0.01	a_1 C–H str	3269

[a] $K_l = \langle \cos^2 q_l \rangle$, where $i = x, y$, or z, q_l is the angle between the molecular axis i and the laboratory Z axis, and the angle brackets indicate ensemble averaging. The accuracy of the experimental determination of K_l was about ±0.005 unless otherwise noted. [b] opb = out-of-plane bend; rd = ring deformation; ipb = in-plane bend; str = stretch. [c] Reference 25. [d] Raman-active vibrations.[19] [e] These fundamentals appear to be split by matrix effects. The higher frequency peak is given in parentheses. [f] Unpublished results, V. Balaji and J. Michl, calculated at the HF/6311G (2D, P) level. [g] The 1,2- and 1,4-substituted derivatives are produced as a 1:1 mixture using **2**; these assignments are based on polarization data and calculated[25] frequencies.

However, the Raman spectrum does not show the predicted splitting of the a_g fundamentals, and the relative intensities of the Raman lines show no observable temperature dependence over the range 4–6 K in neon and 4–25 K in argon, in contrast to expectations based on the calculations.[17] Very recent calculations of Raman intensities[26] showed that the intrinsic Raman cross sections of both components of the split a_g fundamentals are nearly identical, as anticipated. It was then suggested that slight matrix-induced asymmetry of the double-well potential is responsible for the observation of only one member of each tunneling-split a_g line pair in the relatively noisy Raman spectrum. This line is presumably due to a transition originating in a lowest-energy state, whose wave function is largely localized in the more stable of the two wells. The population of the lowest-energy state, whose wave function is localized mostly in the less stable well, is apparently too small to be detectable in the spectra. The calculations suggest that already a 100 cal/mol difference in the energies of the two rectangular forms would be sufficient to bring this about. Better quality Raman spectra are needed before the issue can be settled.

Polarized IR Absorption. We have used polarized spectroscopy in our study of **1** with two objectives in mind. First, the previously assigned symmetries of the IR vibrations could be verified experimentally. Second, an alignment of **1** with respect to its two in-plane directions could allow the rate of valence tautomerization to be measured by following the rate of loss of dichroism.

It should be possible to orient a sample of **1** in a nondestructive manner similar to that used to orient free-base porphyrin,[27] since the UV absorbing transition of **1** is certainly of the π–π^* type and thus polarized in the plane of the molecule. The photon-induced valence tautomerization of **1**, proceeding through the square-shaped first excited state, would then cause the sample to orient in a manner that distinguishes the two in-plane directions. However, orientation by this mechanism preserves an isotropic distribution of molecular planes and would be observed only if the rectangular forms of matrix-isolated forms of **1** do not interconvert rapidly within minutes or faster at 10 K. If this condition is not fulfilled no permanent nondestructive photodifferentiation of the two in-plane axes of **1** would be observed in the polarized IR absorption experiment. Rapid interconversion of the two rectangular forms would make the two in-plane directions of the molecule indistinguishable on the time scale of the sample preparation. In agreement with the conclusions drawn from the matrix-isolated ^{13}C NMR measurements,[18] we find no detectable permanent photoinduced dichroism. This result also explains why 1:1 mixtures of the 1,2- and the 1,4-dilabeled derivatives are always observed. Clearly, these experiments need to be repeated on a much shorter time scale.

The negative result such as the above always leaves a shadow of doubt, and one wonders whether some other mechanism, such as molecular rotation in the matrix, might not be responsible for the absence of observable dichroism in the above experiment. To eliminate at least this one objection, it was therefore important to find conditions under which lasting dichroism can be induced. If the two Kekulé forms indeed interconvert rapidly, this would require a molecular alignment in which the molecular plane distribution is not isotropic.

We find that the use of linearly polarized 248-nm light in the photofragmentation of matrix-isolated anhydride **2** permits the accumulation of permanently dichroic and thus permanently partially aligned **1** by destructive photoselection (Figure 3).[18] The out-of-plane bending vibration is observed to have positive dichroism, while all in-plane vibrations are observed to have negative dichroism. This result confirms the assignment of the 576-cm^{-1} vibration in the unlabeled species to the out-of-plane polarized b_{3u} transition. The degree of dichroism observed for all in-plane polarized IR peaks was always the same, regardless of their assignment as b_{1u} or b_{2u}, under all conditions of irradiation, in agreement with the postulate of rapid tunneling between the two valence tautomeric forms. Representative orientation factors are collected in Table I.

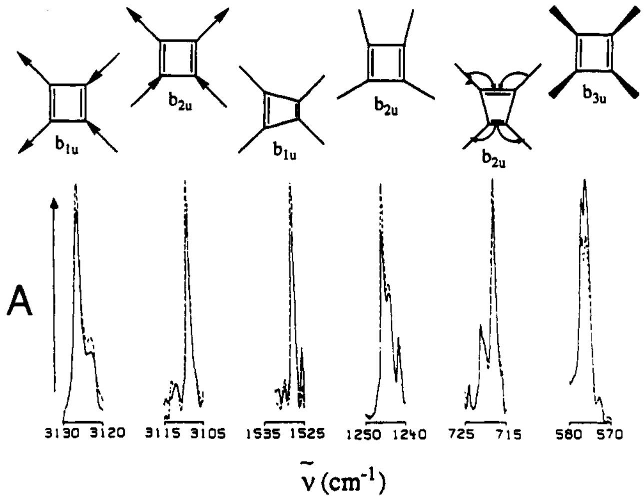

Figure 3. Polarized FTIR spectra of **1**. The photoorientation was achieved by irradiation of matrix isolated **2** with 248-nm light polarized along *Z* (—, IR electric vector parallel to Z, - - -, perpendicular to *Z*).

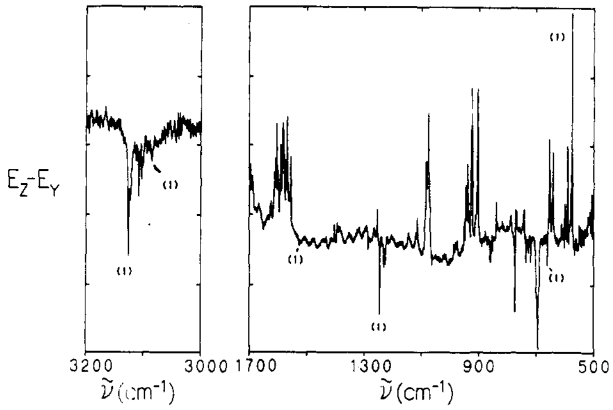

Figure 4. Polarized FTIR difference spectrum of **1**. The photoorientation of **1** was achieved by irradiation of matrix isolated **2** with 248-nm light linearly polarized along *Z*. The spectrum shown is the difference between the absorbance polarized parallel to *Z* and perpendicular to *Z*. The unlabeled peaks belong to oriented **2**–**5**, acetylene, and CO_2.

The other photoproducts, namely CO_2 and **3**–**5**, are also oriented, as is the acetylene photoproduct from the fragmentation of **1**. This is shown in Figure 4. Since the photochemistry of the anhydride is more complicated than we originally hoped, it is not certain that the observed orientation results from photoselection on the anhydride or from production of **1** from another source, such as **5**. It is also possible in principle that the observed dichroism originates from the destruction of **1** itself. This possibility was probed by linearly polarized 248-nm irradiation of a matrix of **1**, produced from **2** by irradiation with 248-nm light, and bleaching of the byproducts with 254- and 313-nm light. Using 248-nm light, **1** is fairly efficiently converted to acetylene.

However, at no degree of conversion was dichroism of **1** or acetylene observed. The highest degree of dichroism of the acetylene would be expected at low degrees of conversion. Since large amounts of acetylene are produced by the bleaching process prior to the irradiation with linearly polarized light, and these bands shift in frequency depending upon their matrix partners, the dichroism of the acetylene IR peaks could easily be masked by the already present acetylene peaks. The absence of preferential alignment of the plane of the remaining **1** away from the *Z* direction is more difficult to account for, and we do not have a good explanation.

Deposition of the labeled precursors and irradiation with linearly polarized 248-nm light produced partially oriented samples of labeled **1**. Only the isotopic purity of **2**-d_1 was insufficient to produce useful polarized spectra. The orientation factors of the labeled samples, taken at a particular degree of conversion, are collected in Table I. As with the unlabeled **1**, only the symmetry of all out-of-plane vibrations can be confirmed experimentally while all of the in-plane vibrations always show the same dichroism. As was dicussed for the parent **1**, the valence tautomerization must be slow on the IR time scale but fast on the time scale of sample preparation for these labeled derivatives as well.

Complexation Effects on IR Spectra. Since most direct observations on **1** have been performed under conditions of isolation in a rigid matrix or a glass, it is important to ask to what degree the environment affects the properties of this unusual molecule. In addition to the general effect of a solvent such as solid argon, one needs to be concerned particularly about the interaction between **1** and the byproducts resulting in its photochemical preparation. These byproducts often share the same cage in the matrix, even if they are not particularly bound to **1**. Indeed, there is no firm evidence for the existence of true bound complexes between **1** and other small molecules, other than normal weak van der Waals complexes, and matrix softening generally causes the contact of the two species to break: they diffuse apart even at extremely low temperatures.

As mentioned already, and discussed in more detail here, the presence of weak intermolecular interactions with the photochemical byproducts in matrices and glasses wrought havoc with the initial IR assignments and caused confusion in UV assignments as well. Of particular interest is the bending fundamental of CO_2. When CO_2 is deposited in argon ($\sim$1:5000) at 10 K this band is split into two peaks at 664 and 662 cm^{-1}, shifted slightly from the gas-phase value of 667 cm^{-1}. The CO_2 that is generated after irradiation of argon matrix isolated **5** exhibits one IR band at 660 cm^{-1} and another at 653 cm^{-1}. Isotopic labeling experiments[28] leave no doubt that both peaks belong to CO_2 and cannot be attributed to **1** as was previously believed. Similar results are obtained using the anhydride **2** as the photochemical precursor.[10] In principle, the observed splitting of this bending fundamental could be due to the CO_2 existing in two different matrix environments, or to a splitting of the degenerate vibration by a symmetry-lowering interaction with a neighbor even if all the CO_2 molecules have the same matrix environment.[28]

Our bleaching and polarization results show that the latter is correct. Since both bands attributed to CO_2 decrease in intensity at the same rate while two new bands appear when the **1** is destroyed, as shown in Figure 5, the appearance of two bands cannot be attributed to different environments. The polarized spectrum, shown in Figure 6, indicates that these bands have different dichroism and that the transition moments appear to be polarized at 90° to each other. These results prove that the degenerate vibration is split and that the effect is not due to differing matrix sites.

The b_{3u} out-of-plane bend of **1** shows a splitting of the order of 15 cm^{-1} and the labeling experiments[28] referred to above demonstrate that the 576-cm^{-1} band is due to free **1** and the 591-cm^{-1} band to **1** perturbed by a molecule of CO_2. Much smaller splittings are observed for in-plane vibrations. When the matrix is warmed to 39 K, the position of the 591-cm^{-1} band reversibly shifts to lower frequency, as shown in Figure 7. Bands of free **1** appear to be unchanged by this temperature increase. The intensity of the 591-cm^{-1} band decreases over time, while that of the 576-cm^{-1} band increases (Figure 8). A correlation of this behavior with the simultaneous changes in the intensities of the peaks assigned to CO_2 leaves little doubt that the assignments to **1**–CO_2 contact pair (591 cm^{-1}) and to free **1** (576 cm^{-1}) are correct.

When **2** is irradiated in Ne at 4 K with 248-nm light, only the band of free **1** is observed although it is now slightly shifted to 574 cm^{-1} (Figure 9). Presumably, Ne is softer at 4 K than Ar at 10 K, allowing diffusion of the CO_2 to occur after the photochemical event. Possibly Ne is small enough to separate the molecules of CO_2 and **1**, preventing the "complex" from being formed. Thus, matrices of **1** free of the CO_2–**1** complex may be produced by cautious annealing of an Ar matrix or by using Ne as the matrix material instead.

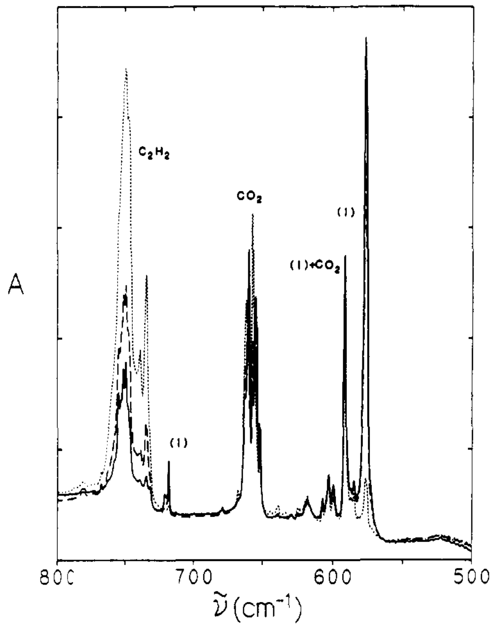

Figure 5. FTIR spectra showing the bleaching of **1**. Both of the bands attributed to CO_2 are bleached at the same rate while the bands due to "free" and "complexed" **1** are bleached at different rates. The spectra were taken after 0 h (—), 12 h (- - -), and 36 h (· · ·) of irradiation with 350–420-nm light from a Xe lamp.

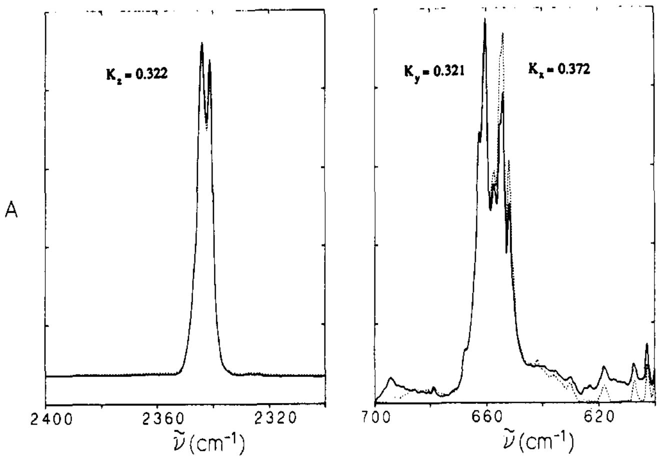

Figure 6. Polarized absorption spectra of CO_2 photooriented by irradiation of **2** with 248-nm light linearly polarized along Z (—, absorbance polarized parallel to Z; - - - perpendicular to Z). The orientation factors K_i are shown (for definition, see Table I).

There have been several attempts to calculate the preferred geometry and binding energy of complexes of CO and CO_2 with **1**.[29] In view of the known difficulty of such calculations,[30] the results are not considered very meaningful. At any rate, all the authors agree that if there is any binding at all, it is very weak. Our results indicate that in a matrix the interaction is repulsive.

Complexation Effect on the Photodecomposition Efficiency. The interaction with CO_2 in the matrix does lead to an interesting effect, however. When a matrix that contains both "free" and "complexed" **1** is irradiated with 350–420-nm light, the band of free **1** is bleached to acetylene at a much faster rate than that attributed to the complexed **1**, as shown in Figure 5. This allows a matrix of only the "complexed" **1** to be produced. Presumably, the presence of the CO_2 molecule permits a much faster heat loss to the matrix environment and thus quenches the hot ground state fragmentation of **1**. This also proves the correctness of the claim made in the discussion of the UV–visible spectra, namely,

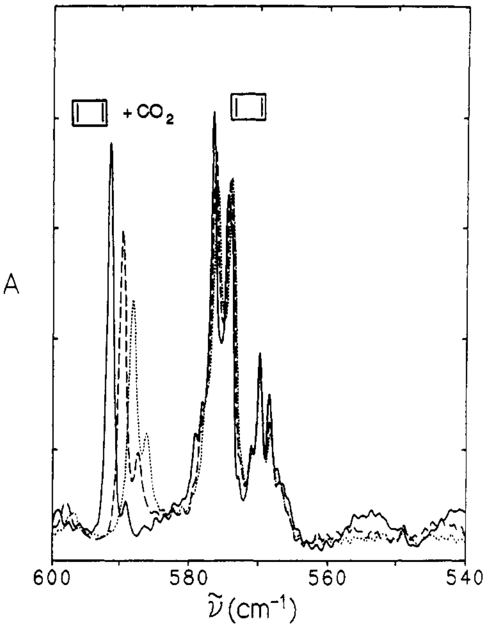

Figure 7. FTIR spectra showing the effect of temperature on the frequency of the perturbed out-of-plane bend of **1**. The spectra were taken at 12 K (—), 22 K (- - -), and at 39 K (· · ·).

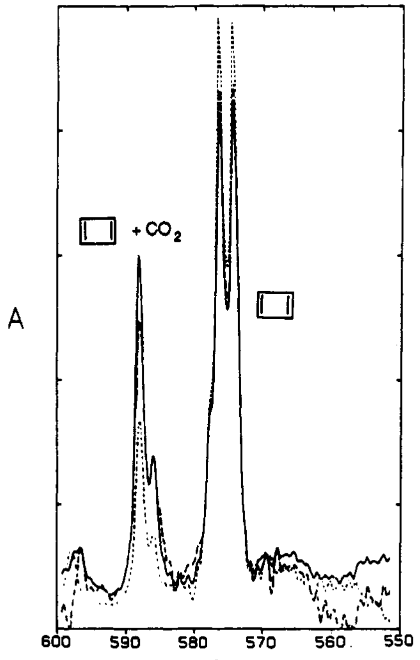

Figure 8. FTIR spectra showing the effect of annealing on the out-of-plane vibrations of **1**. The perturbed band at 587 cm^{-1} disappears over time while the band at 576 cm^{-1} increases in intensity. The spectra were taken at 0 h (—), 12 h (- - -), and 32 h (· · ·) at 39 K.

that the complexed form of **1** is not easily destroyed by these wavelengths.

Conclusions

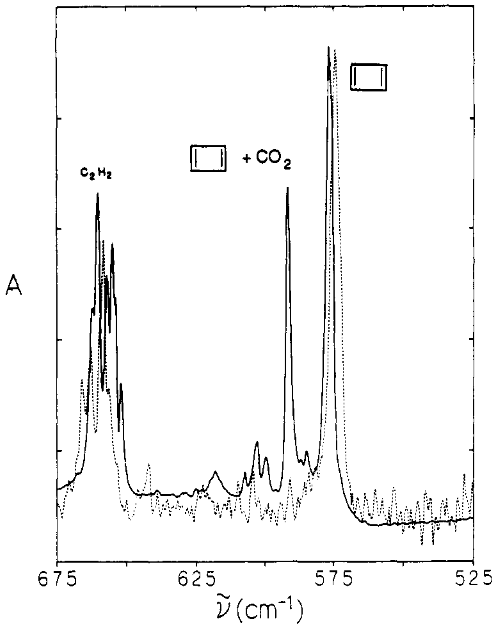

Figure 9. FTIR spectra of the out-of-plane bend region of **1** in argon (—) and neon (· · ·) matrices at 4 K.

Several new results for cyclobutadiene and six of its isotopomers have been obtained. (i) Above a strong onset below 250 nm, the UV absorption spectrum has only a weak tail and no peaks. (ii) The number of observed IR vibrations has been increased considerably, and their in-plane or out-of-plane polarizations have been measured. Raman measurements on labeled **1** are needed before a force field can be established reliably from the experimental data. (iii) Several lines of evidence have been obtained in favor of rapid equilibration between the two Kekulé forms on the time scale of minutes even at 10 K. A partial alignment of the molecular planes induces permanent dichroism of equal magnitude for all in-plane polarized transitions, an isotropic distribution of the molecular planes does not permit permanent dichroism even under conditions expected to differentiate between the two in-plane axes, and the 1,2- and 1,4-doubly labeled isotopomers are always observed in equal amounts. This result agrees with independent matrix-isolation NMR evidence[18] and with results of calculations,[17] but the actual rate of the fast interconversion in the cold matrix environment remains unknown. Surprisingly, no alignment of the planes of the remaining molecules of **1** is observed when its isotropic matrix sample is partially destroyed by irradiation with linearly polarized 248-nm light. (iv) Some of the previously puzzling spectral effects of the presence of a CO_2 molecule in the cyclobutadiene matrix site have been elucidated. A curious inhibition of the photodecomposition of **1** in the presence of CO_2 in the matrix site has been observed and attributed to an enhancement of vibrational relaxation in competition with the fragmentation of the hot molecule.

Acknowledgment. This project was supported by the National Science Foundation (CHE 9020896).

References and Notes

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