Polarization Spectroscopy and ab Initio Study of Photooriented Matrix-Isolated Isotopomers of Phthalic Anhydride. Assignment of the Infrared Absorption Spectrum

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In this paper we provide an assignment of symmetries for all transitions observed in the infrared spectrum of phthalic anhydride (1a), based on data determined from polarization studies of photooriented 1a. Photoselection, using two electronic transitions in phthalic anhydride 1a, at 34 083 and 40 650 cm⁻¹ and of A₁ and B₂ symmetry, respectively, produced two differently oriented uniaxial samples of the anhydride immobilized in neon and other noble-gas matrices. Subsequent polarization measurements in the infrared region, combined with polarized Raman data, allowed a complete determination of transition moment directions for all observed fundamental vibrations. To facilitate definitive spectral assignments, we studied three isotopomers of 1a: $1,2^{-13}$ C-labeled phthalic anhydride (1b), the perdeuterated phthalic anhydride (1c), and the α -¹³C-labeled compound (1d). Absolute infrared absorption intensities were determined for all observed transitions utilizing absolute infrared absorption intensities of CO and CO₂, formed in equimolar amounts with *o*-benzyne (2) in phototransformations of 1. Interpretation of the experimental results and the final assignments were aided by quantum mechanical modeling at the SCF/6-31G** level.

Introduction

Assignments of IR spectra are usually made on the basis of transition energy, absorption intensity, and frequency shifts induced by specific isotopic labeling. The process is essentially a mapping of observed transitions onto a set of theoretically predicted transitions. While most large scale ab initio methods provide reliable energies and intensities for vibrational transitions in small molecules,¹ such results become much less accurate in the case of large molecules, in particular for the intensities. For even larger molecules, such as many molecules of biological interest, meaningful ab initio calculations of their vibrational spectra are presently not possible at all.

In addition to the transition energy and intensity, a very strong assignment criterion for individual transitions is the transition moment direction. However, it is only rarely used, primarily because of lack of insight into the experimental possibilities that might provide such information. As for intensities, a quite sophisticated theoretical treatment is required for accurate predictions of transition moment directions even in small, lowsymmetry molecules.² In contrast, experimental techniques are available which make it possible to determine electronic or vibrational transition moment directions for many molecules. Particularly simple cases are planar molecules, especially those of D_2 , $C_{2\nu}$, or D_{2h} symmetry. In these cases, the directions of transition moments coincide with the molecular symmetry axes; thus they can be properly estimated by simple theoretical methods, and an experimental determination is less demanding. A convenient experimental procedure for obtaining such information uses linearly polarized light in the spectroscopic measurements, which are performed on partially or perfectly aligned molecular samples. Such samples may be produced by dissolving the sample molecules in anisotropic media (i.e.,

crystals, liquid crystals, and stretched or extruded polymers) or by photoselecting an at least partially aligned subset of an isotropic sample (photoorientation).³ While the use of liquid crystals and, especially, stretched polymers is often simple, the preparation of pure or doped oriented crystals may be quite cumbersome. It requires larger amounts of the compound, and interpretation of the results may be difficult. Samples required for infrared measurements have to be of proper thickness, and the molecular orientation distribution has to be determined, e.g., by X-ray diffraction methods. The data analysis is often complicated by crystal effects. Solid noble gases used as captivating solvents for photooriented molecules have the advantage that they are transparent in very broad spectral regions and interact relatively weakly with the guest molecules. However, the application of the photoorientation method is restricted by the need for a convenient orientation mechanism. Photodissociation, photoisomerization, and photoinduced pseudorotation are the most commonly used phenomena for this purpose, but although it never has been clearly demonstrated, photoinduced rotational diffusion may have the greatest potential for wide applications.⁴

Phthalic anhydride (1a) represents a model molecule of particular interest since definitive assignments of its vibrational transitions are not yet established.^{5,6} In addition, the molecule



has important advantages. Primarily, it is well suited for photoorientation, since it has two nonoverlapping electronic

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transitions polarized in the molecular plane which can be used for selective photodestruction (see below). Furthermore, **1a** can be readily isotopically labeled, and as a closed-shell molecule, it is well suited for quantum mechanical modeling.

The vibrational and electronic transition moments of the $C_{2\nu}$ molecule **1a** are restricted to three directions in the molecule, x, y, and z, defined by its symmetry. Theoretical methods readily provide the proper axis for each transition, but this is not the case for standard experimental methods. So far, transition moments have been experimentally determined for vibrational transitions in a very limited number of molecules, using mostly molecular samples aligned in pure crystals, mixed crystals, liquid crystals, or stretched polymers (for a list of references, see ref 3). Recently, and only in very few cases, photoorientation has been systematically used to extract information on transition moment directions.⁷⁻⁹

Experimental Section

Phthalic anhydrides **1a**-d were sublimed, in separate experiments, at 26-32 °C into a stream of noble gas or N₂ (1-3 mmol/min) and condensed on a cold CsI or sapphire target. The temperature of the spectroscopic window was maintained at a level suitable for high optical quality matrices for each gas (28 K for Ar, 24 K for N₂, and 4.2 K for Ne matrices). During the spectroscopic measurements and laser irradiations, the matrices were kept at about 12 K, except for Ne, for which the lowest temperature attainable with our cryostat, 4.2 K, was necessary at all times. The matrix ratio was determined to be ~1:950 in the samples used for infrared measurements and ~1:300 in the Raman samples. Samples for electronic absorption measurements were ~0.05 mm thick, while the thickness of IR samples varied between 0.2 and 0.5 mm, and Raman samples were ~0.9 mm thick.

The low-temperature samples were prepared using closed cycle refrigerators: either two-stage Displex (12 K) or threestage Heliplex (4.2 k) units (APD Cryogenics). For the photochemical transformations, an excimer laser (Lambda Physik) was used, generating monochromatic light at 248 nm (KrF) or 308 nm (XeCl) and 351 nm (XeF). In some of the experiments, light at 356 nm from an Ar-ion laser (Coherent I-100) or tunable doubled output from a ring dye laser was used. Raman spectra were recorded using a Spex 1401 1m double monochromator and excitation from either an Ar-ion laser or a ring-dye laser working with rhodamine 6G dye. The effective spectral resolution was calculated to be about 5 cm⁻¹.

A uniaxially stretched (500%) polyethylene sample was prepared using the standard method, by soaking the polymer in a chloroform solution of $1.^3$

Polarization spectra were recorded in the infrared region using Nicolet FTIR (SXR-60 and Magna 500) instruments and a Cambridge Physical Sciences polarizer (IPG-225). The resolution was kept at 0.5 cm⁻¹. Typically about 500 scans were coadded. Polarized UV-visible absorption spectra were measured on a Shimadzu instrument using Glan-Thompson polarizers in both the sample and reference beams. Raman depolarization ratios were determined using a sheet polarizer and polarization scrambler at the entrance slit of the monochromator.

Anhydrides 1b-d were obtained using the standard method, by dehydration of the corresponding phthalic acids with acetic anhydride. The acids (phthalic acid-1,2-¹³C₂, phthalic acid-3,4,5,6-d₄, and phthalic acid- α -¹³C (precursor for 1d)) were purchased from MSD in 99% isotopic purity.¹¹

Calculations. The geometry of **1a** was optimized with a 6-31G** basis set at the SCF level using CADPAC.¹² The vibrational frequencies and infrared intensities for 1a-d were



Figure 1. Electronic absorption spectrum of 1a isolated in an argon matrix at 12 K. Polarized electronic absorption spectra of 1a in stretched polyethylene (insert). E_Z (solid line) represents intensity measured along the stretching direction, and E_Y (dashed line) is the intensity measured with the electric vector perpendicular to the stretching direction.

obtained analytically with the same program. Raman intensities were calculated with GAUSSIAN 92.¹³

Results and Discussion

To facilitate an interpretation of the planned photoorientation experiments, we recorded linear dichroism (LD) electronic absorption spectra of 1a dissolved in stretched polyethylene at room temperature. The results are shown as an insert in Figure 1. The fact that the two recorded absorbance curves are almost proportional over a region containing differently in-planepolarized transitions shows that the molecule presents a rare case of an almost "disklike" orientation³ in the stretched polyethylene, with almost identical average angles between all in-plane transition moments in the molecule and the sample stretching direction. Furthermore, since $E_Z > E_Y$ over the whole spectral region, the in-plane axes must be better aligned than the out-of-plane one (see later). Labeling the best aligned axis in the molecule z and the worst x, we find $K_z = \langle \cos^2(M_z, Z) \rangle =$ 0.375 and $K_y = \langle \cos^2(M_y, Z) \rangle = 0.365$. Out-of-plane polarized transitions, which do not occur in the UV spectral region studied, will have $K_x = (\cos^2(M_x, Z)) = 1 - K_z - K_y = 0.26.^3$ Here *u* = x, y, z refer to molecular axes, Z is the stretching direction (the unique sample axis), M_i a transition moment along axis i, and (M_i, Z) the angle between M_i and Z. The brackets indicate averaging over all sample molecules. In the LD spectra shown in the insert in Figure 1, the first band around 300 nm corresponds to K_r and thus has an electronic transition moment in the z direction (is polarized along z), while the second band, around 240 nm, corresponds to a slightly lower K value and is polarized along y.¹⁰ In the present case, the stretched sheet LD spectra are much less useful than in most other cases, due to the near disk shape of the molecule. The much better resolved spectrum of isotropically aligned 1a isolated in an argon matrix before irradiation is presented in the main part of Figure 1. The labeling of molecular axes is shown in the insert to Figure 2; the distinction between the two in-plane axes is clear from any assignment of an in-plane UV or IR transition.

In the subsequent photochemical transformations, isotropic samples of 1, isolated in noble-gas matrices at temperatures ranging from 4 to 12 K (see the Experimental Section), were irradiated with vertically linearly polarized light. Some samples were irradiated at 308 nm, corresponding to the electronic



Figure 2. Infrared absorption spectrum of 1a isolated in a neon matrix at 4.2 K. Labeling of the molecular axes is presented in the insert. The out-of-plane transitions are along the x axis (not shown in the insert). All bands are marked with appropriate polarizations. Peaks belonging to trace amounts of H_2O are crossed out.

transition polarized along z, and others at 248 nm, corresponding to the y-polarized transition. In both cases, the irradiation led to the conversion of 1a, 1b, or 1c into CO, CO_2 , 2, and 3.⁶ In the first case, molecules with their z axis inclined at small angles with respect to the electric vector of the light, Z, had a greater probability of being converted. This follows from the fact that the probability of absorption of Z-polarized photons by transition along molecular axis z, and thus also the phototransformation in the excited state, is proportional to $\langle \cos^2(\mathbf{Z},z) \rangle$, where, as before, (\mathbf{Z},z) is the angle between the z axis in each individual molecule and Z, and the brackets indicate an average over all molecules in the sample. As a result, the population of the original molecules with small values of angle (\mathbf{Z},z) was depleted. In the second case, irradiation at 248 nm preferentially converts molecules with their y axes forming small angles with the direction of the electric vector, Z (probability proportional to $\langle \cos^2(\mathbf{Z}, y) \rangle$).

Irradiation at 308 nm is particularly convenient, because the photochemical products 2 and 3 absorb light only very weakly at this wavelength. The degree of alignment of the remaining anhydride molecules will increase, as the conversion of 1 advances, and a highly aligned sample may be produced.³ However, the price paid for high alignment is a low concentration of 1a. Substantial absorption of light at 248 nm by 2 prevents generation of samples that are as well aligned when irradiation is performed at this wavelength.

The products of the two photoselection experiments are two different samples of partially aligned molecules. Both alignments are uniaxial around \mathbb{Z} , and the two samples exhibit linear dichroism in the infrared and UV-visible regions. In both cases of irradiation wavelengths, absorption of vertically (\mathbb{Z}) polarized infrared radiation, $E_{\mathbb{Z}}$, will be weaker than that of horizontally (\mathbb{Y}) polarized radiation, $E_{\mathbb{Y}}$, for transitions with the same transition moment direction as that of the transition which was used for the photoselection. This is called negative linear dichroism ($E_{\mathbb{Z}} - E_{\mathbb{Y}} < 0$). For transitions with the other two moment directions, a positive linear dichroism ($E_{\mathbb{Z}} - E_{\mathbb{Y}} > 0$) will be observed.

A simple quantitative description is possible.³ The orientational properties of interest, also in connection with absorption spectra of the photooriented samples, are the average cosine squares of the angles between the molecular axes, x, y, and z, and the unique sample axis Z, earlier referred to as the K values (orientation factors): $K_{\mu} = \langle \cos^2(Z, \mu) \rangle$, $\mu = x$, y, z. By definition $K_x + K_y + K_z = 1$. In the isotropic sample there is no difference between the alignment of the three axes and all K's are equal to 1/3. The irradiation at 308 nm and the resulting



Figure 3. Segment of the linear dichroism difference spectrum ($E_Z - E_Y$), determined from polarized infrared absorption measured after polarized irradiation at 308 nm of Ar matrix-isolated **1c** (top), and after polarized irradiation at 248 nm (bottom). Bands originating from **1c** are marked with the appropriate polarizations, determined according to Table 2. Unmarked bands belong to **2c** and **3c**.

 TABLE 1: Expected LD Signs for Electric Dipole

 Transitions

	transition moment along \rightarrow						
	x	у	z				
stretched polymer sheet irradiation at 308 nm irradiation at 248 nm	- + +	+ + -	+ +				

depletion of the population with low values of angle (\mathbb{Z} ,z) will produce a new $K_z = K_{lz}$ with a value below 1/3; since $K_y = K_x$ = $(1 - K_z)/2$, we have $K_{ly} = K_{lx} > 1/3$.

Similarly, the irradiation at 248 nm and depletion of the population with low values of angle (\mathbb{Z} ,y) will produce a $K_{2y} < \frac{1}{3}$ and $K_{2x} = K_{2z} = (1 - K_{2y})/2 > \frac{1}{3}$.

These results can be summarized in a simple table, in terms of expected signs of infrared linear dichroism $(E_Z - E_Y)$ for transitions polarized along x, y, and z axes (Table 1).

It is simple to show that experimentally determined dichroic ratios for nonoverlapping transitions *i*, $d_i = E_Z^i / E_Y^i$ are related to the orientation factors: $K_i = d_i / (d_i + 2)$.³

Numerous sets of polarized infrared absorption spectra were obtained at various degrees of photochemical conversion for each of the three isotopomers. For each we have selected the pair of polarized spectra which have the best alignment, and at the same time a good signal-to-noise ratio, and used them for the spectral assignments. Examples of such spectra, obtained after irradiation of 1c at 308 and 248 nm, are shown as a difference between the observed spectra E_Z and E_Y (the linear dichroism) in Figure 3.

The experimental results of IR LD for 1a-c are presented in Figures 2, 4, and 5, in a form of simple infrared absorption spectra of these compounds isolated in neon matrixes, with measured polarizations marked above each peak. They are compiled in Table 2. Table 2 also contains results of quantum mechanical modeling calculations at the SCF level employing 6-31G** basis set. The calculated results are also presented in Figures 6 and 7. They are sorted by symmetry species for easier visual comparison with experimental data. The optimized equilibrium geometry of 1 is presented in Figure 8.

Table 2 was constructed in the following way: theoretically predicted vibrations of **1a** were separated into three groups corresponding to the infrared active symmetry species. The



Figure 4. Infrared absorption spectrum of 1b isolated in a neon matrix at 4.2 K. All bands are marked with appropriate polarizations. Peaks belonging to trace amounts of H_2O are crossed out.



Figure 5. Infrared absorption spectrum of 1c isolated in a neon matrix at 4.2 K. All bands are marked with appropriate polarizations. Peaks belonging to trace amounts of H_2O are crossed out.



Figure 6. Calculated infrared absorption spectrum of 1a. Labeling of the symmetry axes is indicated in the insert; the out-of-plane direction x forms a basis for b_1 . All calculated frequencies are scaled by a factor of 0.91 in this plot.

planar anhydride molecule belongs to the $C_{2\nu}$ point symmetry group, and its 39 normal vibrational modes can be classified into the following symmetry types:

$$\Gamma_{\nu} = 14a_1 + 6a_2 + 6b_1 + 13b_2$$

While all of the symmetries are allowed in Raman spectroscopy, only a_1 , b_1 , and b_2 vibrations will be active in infrared



Figure 7. Calculated infrared absorption spectrum of 1c. All calculated frequencies are scaled by a factor of 0.91 in this plot.



Figure 8. Optimized at SCF/6-31G** equilibrium geometry of 1.

absorption. For each symmetry class, frequencies were arranged in decreasing order. Correlation of these frequencies with those of 1b is simple due to the minute changes of the normal modes caused by the introduction of the two ¹³C in the particular positions 1 and 2. These replacements cause the smallest possible perturbation in anhydride vibrations, affecting only few modes to a larger degree. A single ¹³C label lowers the symmetry of the molecule¹¹ to C_s , and replacement of any other pair of carbons would, according to our calculations, cause larger changes in normal modes of anhydride. Because of the relatively small but measurable changes in the normal modes, both frequencies and intensities for all vibrations are affected only to a small degree, and no anomalous shifts are expected. Therefore, all frequencies, again arranged in decreasing order for each symmetry species, can be easily correlated with those of 1a, as shown in Table 2. Visual inspection of the calculated normal modes for both compounds confirms the correctness of such correlation.¹⁴ We have added a column in Table 2 with the values of the frequency shifts for easier comparison with those obtained from experiment.

Similarly, we have correlated calculated normal modes of 1c with 1a. From inspection of Table 2 it is clear that for three a_1 modes and four b_2 modes, the correlation between the spectra of 1a and 1c is not trivial. In these instances we had to inspect

TABLE 2:	Vibrations	of Phthalic	Anhydride ^a
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	C ₈ H ₄ O ₃								¹² C ₆ ¹³ D ₂ H ₄ O ₃								C ₈ [D ₄ O ₃				
		exptl calcd ^b		exptl calcd ^b						exptl			calcd ^b									
	ν	ĩ	Ι	I ^R	ĩ	I	I ^R	ĩ	Δ	I	ĩ	Δ	Ι	ĩ	Δ	Ι	I ^R	ĩ	Δ	Ι	I ^R	assignment ^c
aı	1	3095	3.0	63 ^d	3088	5.5	223.8	3095	0	3.0	3088	0	5.5	2313	782	2.6	53 ^d	2290	798	4.7	97.7	C-H(D) s
	2	3068	1.6		3070	9.3	106.8	3069	0	1.8	3070	0	9.3	2291	778	1.0		2272	798	5.9	40.9	C-H(D) s
	3	1868	217.0	100	1946	299.0	85.5	1864	4	208.6	1946	0	296.9	1874	6	228.2	100	1946	0	299.5	87.1	C=O s
	4	1616	1.4	14	1645	0.6	8.8	1588	28	1.2	1615	30	0.4	1588	28	1.0		1619	26	1.0	9.0	ring $s(C_{1,5}-C_{2,6} s)$
	5	1451	1.7	1	1491	0.4	1.2	1445	6	1.9	1474	17	2.1	1395	56	32.4		1407	84	43.1	7.8	$C_1 - C_2$ s oph $C_5 - C_6$ s + C - H(D) b
	6	1355	37.0		1329	286.7	23.0	1343	12	32.9	1316	13	317.8	1329	26	16.6		1291	38	291.4	15.8	$C_{1,2}-C_{7,8}$ s iph C_5-C_6 s
	7	1261	272.3	7	1236	125.8	7.5	1248	13	283.0	1227	9	104.8	1228	33	268.5		1188	48	98.2	8.4	Kekulé vibration + $C_{7,8}$ - O_{11} s
	8	1213	4.1	6	1138	17.2	11.4	1202	11	4.3	1124	14	2.0	1068	144	41.0		1077	61	5.8	29.2	$C_1 - C_2$ s oph $C_5 - C_6$ s + $C_{7,8} - O_{11}$ s
	9	1108	66.3	12	1114	20.2	10.6	1096	12	35.2	1107	7	23.7	862	246	4.9	_	848	266	0.4	11.8	$C_5 - C_6 s + C_{3,4} - H_{14,15}(D) b$
	10	1010	6.5	38	1005	0.9	20.8	1009	1	7.0	1004	1	0.9	812	198	5.1	7	811	194	1.4	6.3	$C_{3,5}-C_{4,6}$ s + $C_{3,4}-H_{12,13}(D)$ b
	11	135	0.9	24	731	0.1	14.8	133	2	0.8	129	2	0.1	693	42	1.2	28	691	40	0.1	10.8	$5 \text{mr s} + C_{1,2} - C_{3,4} - C_{5,6} $
	12	633	11.6	14	634	3.6	3.1	632	1	12.0	634	0	3.0	632	1	11.8	14	634	10	3.4	3.5	$C_7 - O_{11} - C_8 b$
	13	253	3.2	13	252	1.5	4.2	352	1	3.7	252	1	1.2	324	9	8.1	11	323	10	1.7	3.0	$\operatorname{omr} S + U = 0 D + U = 0 D$
	14	301	2.2	/	332	15.5	4.5	501	0	2.4	552	U	15.5	330	3	2.0	0	549	3	14.0	4.0	CO IP 0
b ₁	15	964	0.3		1005	0.6	0.5	962	2	0.2	1004	1	0.6	796	168	7.3		826	179	4.0	0.5	$C - H_{12,13}(d)$ op b
	16	790	5.5		813	2.7	0.0	787	3	6.1	809	. 4	3.6	741	49	13.7		763	50	38.0	1.2	5 mr b + CH(D) op b
	17	713	75.5		733	136.3	2.7	711	2	74.3	733	1	135.4	576	137	39.0		592	141	60.0	0.2	C-H(D) op b
	18	394	0.4	1	418	0.6	0.0	393	1	0.3	415	3	0.7					368	50	1.5	0.0	$C_{1,2}-C_{3,4}-C_{5,6}-H_{12,13}(d)$ flopping vibration
	19	221		7	188	0.1	3.5				186	2	0.1	168	3			182	6	0.2	2.6	skeletal b
	20	171		6	158	5.6	0.5				157	1	5.4	168	3		4	157	1	5.5	0.7	skeletal b, C=O op b
b ₂	21	3085	2.2	39 ^d	3085	3.0	12.0	3085	0	2.8	3085	0	3.0	2305	780	2.0	24 ^d	2287	798	5.1	6.1	C - H(D) s
	22	3062	1.5		3057	2.2	58.4	3062	0	1.1	3057	0	2.2	2282	784	0.9		2259	798	1.0	22.2	C-H(D) s
	23	1801	738.0	48	1881	868.8	43.2	1809	-8	752.0	1881	0	868.1	1805	-4	710.0	46	1881	0	867.0	43.2	C=0 s
	24	1605	1.3	17	1646	3.3	45.2	1581	24	1.7	1627	19	5.0	1581	24	1.0		1619	27	1.5	43.7	ring s ($C_{2,3}$ - $C_{4,5}$ s oph $C_{1,4}$ - $C_{3,6}$ s)
	25	1474	22.0	2	1486	18.4	0.3	1464	10	21.7	1475	11	16.6	1377	97	18.3		1387	99	19.3	0.3	$C_3 - C_{1,5}$ s oph $C_4 - C_{2,6}$ s + $C_{1,4} - C_{3,6}$ s)
	26	1286	3.1		1293	3.1	0.5	1275	11	3.0	1279	14	4.3	1131	155	7.4		1135	158	30.8	7.5	C_1-C_7 s oph C_2-C_8 s + iph C-H(D) b
	27	1173	4.3		1174	14.3	7.1	1164	9	5.6	1162	12	16.8	1022	151	9.7		1036	138	133.6	0.4	$C_1 - C_7$ s oph $C_2 - C_8$ s + oph $C - H_{12,13}(D)$ b
	28	1074	1.1		1084	4.9	0.4	1066	8	3.4	1077	7	13.7	866	213	15.9		862	222	0.2	2.5	$C_1 - C_3 - C_5 b \text{ oph } C_2 - C_4 - C_6 b$
	29	914	316.0	3	1029	255.1	2.0	913	1	309.0	1027	2	242.5	910	4	282.0		1009	20	105.3	1.5	$C_7 - C_{11}$ s oph $C_8 - C_{11}$ s
	30	839	0.3	_	838	2.1	1.7	838	1	0.4	837	1	2.1	800	39	16.8		799	39	6.9	0.3	$C_3-C_5-C_6$ b oph $C_5-C_6-C_4$ b + C_1-C_7 s oph C_2-C_8 s
	31	678	18.1	2	677	2.4	0.2	671	7	18.5	670	7	2.6	658	20	15.9		657	20	1.8	0.2	ring det $+ C - O b$
	32	535	22.2	-	538	6.4	1.6	532	3	23.2	534	4	6.3	522	13	27.4		521	17	5.0	2.0	skeletal s along C_6-C_7 and C_5-C_8 axes
	- 33	270	0.7	- 7	246	1.4	1.7	269	1	0.9	245	1	1.4	257	- 13	0.7	6	237	9	1.5	1.5	skeletal det

^{*a*} Neon matrix (IR), and argon matrix (Raman); $\tilde{\nu}$, in cm⁻¹, *I*, absolute intensity in km/mol; *I*^{*R*}, Raman isotropic relative intensity (exptl), and Raman absolute intensity in Å⁴/amu (calcd); all observed and calculated isotopic shifts (Δ , in cm⁻¹), are to the red, except for C=O stretches. ^{*b*} SCF/6-31G^{**}. All calculated frequencies are scaled by an arbitrary factor of 0.91. ^{*c*} Approximate mode description (see text); op = out-of-plane, ip = in-plane, b = bend, s = stretch, def = deformation, 5mr = five-member ring, 6mr = six-member ring, iph = in-phase, oph = out-of-phase; numbering of atoms is shown in Figure 8. ^{*d*} Components of the pairs: ν_1 , ν_2 and ν_{21} , ν_{22} were not separated in the Raman spectrum.

 $\begin{array}{c} 2000 \\ 600 \\ \\ 600 \\ \\ \\ 300 \\ \\ 2000 \end{array}$

Figure 9. Raman spectrum of 1a isolated in argon matrix at 12 K. Excitation at 603 nm (ring dye laser, R6G), P = 790 mW. Totally symmetry vibrations are marked with full circles, and non-totally-symmetric vibrations with empty circles.

the displacements of all atoms, along the normal coordinates, in order to establish proper correspondence of the modes. This is equivalent to comparing the appropriate dominant contributions to the diagonal potential energy distribution.

Computational results, presented for **1a** and **1c** in Figures 6 and 7, were then used as a guide for correlating the observed spectra. The calculated normal-mode symmetry and the observed vibrational polarization, frequency, frequency shift induced by isotopic labels, and intensity were used as the assignment criteria. For several weak far infrared vibrations, we have utilized frequencies and polarization data from the Raman spectra; an example is shown in Figure 9. However, no attempt was made to make a complete assignment of such spectra. We hope that Raman polarization studies of photooriented anhydrides, currently in progress, will make it possible to differentiate between three types of non-totally-symmetric vibrations and completely analyze the vibrational spectrum of this molecule.

The vibrational results are compiled in Table 2. For each of the isotopomers we have observed over 120 infrared absorption bands; among these, 33 were assigned as fundamentals in Table 2, using the criteria mentioned above. All of the 33 infrared active fundamentals predicted by theory were thus accounted for in experimental spectra. Many combination and overtone bands were observed outside the normal region of fundamental absorptions. A few cases where the choice was not clear will be discussed below. We had to reassign eight bands, which in previous studies were assigned as fundamental vibrations either because we observed them with different symmetries than those assumed in earlier assignments or because the isotope shift pattern for the earlier assignments did not agree with our theoretical predictions.⁵

We have determined the absolute absorption intensities, for all observed infrared active transitions in **1a**-c, in the following way: IR absorption spectra for the isotropic sample, equivalent to: $(2E_{\rm Y} + E_{\rm Z})/3$, were obtained for each of the anhydrides; integrated intensities of each observed transition were compared with those of CO₂ and CO formed in equimolar quantities in the subsequent photochemical transformation to **2**. Earlier, in separate experiments, absolute intensities for CO₂ and CO were determined using a standard quartz microbalance and He-Ne laser interference techniques.¹⁵ We found the following values for CO₂: ν_I (2348 cm⁻¹), $I = 485 \pm 15$ km mol⁻¹, and ν_2 (661 cm⁻¹), $I = 62 \pm 2$ km mol⁻¹. For ν_I of CO at 2141 cm⁻¹, we

Figure 10. Segment of the infrared absorption spectra of 1a isolated in a neon matrix at 4.2 K (bottom), in an argon matrix at 12 K (center), and in a Xe matrix at 12 K (top), showing congested region of carbonyl stretches.

found $I = 64 \pm 2$ km mol⁻¹. All experimental absolute intensities listed in Table 2 are believed to be accurate to $\pm 5\%$ or better.

Vibrations of a₁ Symmetry. We have selected from over 70 observed z-polarized vibrations the best candidates for the 14 fundamentals of a₁ symmetry, based on their transition moments, frequencies, isotopic shifts and intensities, and assigned them as a_1 fundamentals. The two C-H symmetric stretches, weakly active in the infrared, were not affected by 13 C labeling and were shifted by a factor of 0.75 (0.74) calculated) in the perdeuterated compound. The exact position of symmetric carbonyl stretch vibration v_3 is somewhat ambiguous due to Fermi resonances.¹⁶ There are several combination bands which might couple with v_3 and split it via Fermi resonance. The most likely candidates are as follows: v_6 + $v_{12} = 1894 \text{ cm}^{-1}; v_7 + v_{13} = 1887 \text{ cm}^{-1}; v_8 + v_{13} = 1869$ cm⁻¹; $v_9 + v_{11} = 1843$ cm⁻¹ (after correction for anharmonicity, the actual frequencies will be lower). They are, to a large degree, responsible for the complex band structure observed in this region.

Over 30 bands are observed between 1750 and 1900 cm^{-1} . Conceivably, some components may be due to the isolation of 1 in different matrix sites, but the spectrum is not simplified much by matrix annealing. The different appearance of these bands in various matrices, as shown in Figure 10, is caused by small frequency shifts of the fundamentals, which may substantially change their coupling with v_3 . Interestingly, v_3 does not interact with the first overtone of the very strong v_{29} (2 v_{29} $= 1828 \text{ cm}^{-1}$), because of a too large frequency difference. This overtone is observed for **1a** in a Ne matrix at 1808 cm^{-1} ; it is polarized along the z axis, and it shifts down in 1c, as expected, to 1803 cm^{-1} . The possible alternative assignment of this band as a combination of v_7 and v_{14} ($v_7 + v_{24} = 1812$ cm⁻¹) is not viable, because of the much larger isotopic shift expected in 1c. For each isotopomer, 1a-c, we have arbitrarily selected the strongest component of such multiplets and assigned them as "fundamentals". Since most of the intensity in this cluster of bands originates in ν_3 , integration over all components leads



to absolute intensities for the C=O stretch in good agreement with quantum mechanical predictions. The $v_4 - v_5$ vibrations do not require much comment. The choice of v_6 from the recorded spectrum is based on its frequency match rather than intensity, which differs by an order of magnitude from those calculated for 1a-c. According to intensity criterion, the observed set of bands which we ascribed to the calculated mode v_7 would be a much better choice for v_6 , because they are the most intense z-polarized transitions. Both v_7 and v_8 are split by Fermi resonances. While the two observed components of ν_7 , at 1355 and 1337 cm⁻ are most likely the result of interaction with $2v_{31}$, the observed quartet structure of v_8 (1251, 1261, 1266, and 1268 cm⁻¹) might be a result of resonance with $2v_{12} =$ 1266 cm⁻¹, and $v_{11} + v_{13} = 1268$ cm⁻¹. In 1c the overtone of v_{12} is shifted and no longer available for resonance with v_7 , thus its simpler shape.

The agreement between observed and calculated frequencies and isotopic shifts for $\nu_9 - \nu_{12}$ and ν_{14} is remarkably good, and assignments are very secure. The assignment of the extremely weak ν_{11} as a fundamental in the infrared is based on its strong activity and proper polarization in the Raman spectrum of **1a** and **1c**. Similarly, a weak ν_{13} vibration, which closely overlaps ν_{32} of b₂ symmetry, was assigned as a fundamental on the basis of its polarization in both the infrared and Raman spectra. In the Raman spectrum ν_{13} , is definitely polarized ($\varrho = 0.3$) and has substantial intensity ($I^R = 13$). Additional support for this assignment came from the data obtained for **1d**, where the band is separated from ν_{32} by a few additional wavenumbers, in accordance with theoretical predictions.

Vibrations of b₁ Symmetry. In the b₁ symmetry class, all six modes predicted by theory are accounted for in the experimental spectra. The very weak x-polarized band observed for **1a** at 964 cm^{-1} , together with its counter partners in **1b** and 1c, fits very well the prediction for v_{15} fundamental and was assigned accordingly. The intensity of a very weak v_{17} in 1a and 1b, which is predominantly $C-H_{12,13}(D)$ out-of-plane bend, increases significantly in 1c, as anticipated by theory. By far the strongest peak, v_{17} , can easily be assigned as an out-ofplane C-H(D) bending vibration. It is coupled with the carbonyl out-of-plane bend. It shifts in 1c by a factor of 0.81 (calculated 0.81), and its intensity decreases by a factor of 1.9 (calculated 2.3); the observed absolute intensity values differ by 50% from the calculated ones. For ν_{17} , the observed isotopic shifts as well as the substantial intensity increase in 1c further confirm the assignment. The two lowest frequency vibrations, v_{19} and v_{20} , were outside the range of our FTIR instrument and were observed only in the Raman spectrum (Figure 9). Both had depolarization ratios very close to 0.75. Still, their assignment as b₁ fundamentals is quite secure, because no other fundamentals nor combinations are predicted in their immediate vicinity. In accordance with calculations, which predict only one b_1 fundamental below 200 cm⁻¹, we assigned an absorption at 171 cm⁻¹ as a ν_{20} fundamental, and a weak band at 394 cm⁻¹ in **1a** as a ν_{18} fundamental.

Vibrations of b₂ Symmetry. In the b₂ symmetry class, we assigned 13 *y*-polarized observed infrared transitions to the predicted 13 fundamental modes. The very weak C-H(D) stretches, being well separated from other fundamentals, are easily assigned. Again, observed shift factors (0.75) for both asymmetric stretches between **1a** and **1c** agree very well with those predicted by theory (0.74). Despite their weakness, their observed intensities are also in good agreement with theory. v_{21} was reassigned from the previously reported 3059 to 3085 cm⁻¹ on the basis of its polarization and agreement with the calculated frequency. The choice of frequency of the asym-

metric carbonyl stretch fundamental is again somewhat arbitrary due to the strong Fermi coupling with combination bands, while its observed intensity is in excellent agreement with the calculated one. In this case the most likely combinations which could participate in resonance with ν_{23} are as follows: ν_{9} + $v_{31} = 1789 \text{ cm}^{-1}$; $v_6 + v_{32} = 1796 \text{ cm}^{-1}$; $v_{12} + v_{27} = 1806$ cm^{-1} ; $v_{13} + v_{26} = 1818 cm^{-1}$. A somewhat simpler structure of this band in 1c can be explained as a result of fewer combinations available for Fermi resonance, due to the frequency shifts of the participating fundamentals. The assignments of $v_{24} - v_{26}$ and $v_{30} - v_{33}$ require little comment. We had to reassign v_{24} and v_{26} compared with earlier studies in order to obtain much better agreement for frequency and isotope shifts. We did not observe any y-polarized absorption around 410 cm⁻¹ in our spectra; intensity at this frequency was previously assigned as a v_{32} fundamental.⁵ Instead, we are convinced that the strong y-polarized vibration at 535 cm^{-1} in **1a** should be assigned to this (v_{32}) b₂ fundamental. Both its frequency, intensity and isotopic shifts fit perfectly with theoretical predictions. A very strong v_{29} (C-O-C stretch) is easily assigned. However, the observed shift of 4 cm^{-1} in 1c, much smaller than the anticipated 22 cm⁻¹, is worth mentioning. This does not agree with the commonly accepted belief that such shifts are very accurately predicted for all normal modes at this level of theory.

Finally, it is worth noticing that the observed frequencies for the majority of in-plane polarized vibrations differ from calculated harmonic frequencies by nearly the same factor; we have used this factor, 0.91, for frequency scaling in Figures 6 and 7 and Table 2.

Conclusions

In this paper we provide a complete symmetry assignment for the infrared active vibrations in phthalic anhydride. Since standard LD experiments in stretched polyethylene sheets did not allow a safe separation of differently in-plane polarized vibrations, we had to design new photoorientation experiments based on photoselection. Using the two excited states of A₁ and B₂ symmetry, irradiation of samples in noble gas matrices led to photodissociation of 1a into 2, 3, CO, and CO₂. Plane polarized 32 468 and 40 323 cm⁻¹ photons produced two differently oriented, uniaxial samples. These were used for polarized infrared absorption measurements, resulting in absolute symmetry assignments for each observed transition. The use of CO and CO₂ as internal absolute intensity standards allowed us to determine absolute infrared absorption intensities for all observed transitions. For strong or noncoupled modes, the agreement with theory is good, while for most other bands it is fair at best. This shows the limited value of calculated intensities for spectral assignments, at least of those obtained with currently available methods. Finally, use of isotopomers 1b and 1c combined with moderate quality quantum mechanical modeling further enhances the reliability of the assignments. Our results were in disagreement with previous assignments of eight bands out of the 33 fundamentals, but it was possible to safely reassign these eight. This demonstrates the power of our approach, in particular the use of experimentally determined transition moment directions, supplemented with studies of isotope shifts and, to a lesser degree, intensities, provides safe spectral assignments.

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(10) Strong vibronic activity is observed in the lowest energy electronic transition of **1a** as can be seen from Figure 1. In an argon matrix (bottom), at 12 K, we find $\lambda_{max} = 293.4$ nm (34 083 cm⁻¹); it shifts to $\lambda_{max} = 296.6$ nm (33 715 cm⁻¹) in a polyethylene matrix, at RT. The next transition is at $\lambda_{max} = 246.0$ nm (40 650 cm⁻¹) in Ar and at $\lambda_{max} = 248.6$ nm (40 226 cm⁻¹) in polyethylene.

(11) We have recorded polarization spectra for 1d, but they were not analyzed in detail. Carbonyl stretches in 1d, corresponding to v_3 and v_{23} in 1a, appear in the argon matrix at 1849 cm⁻¹ (I = 202 km mol⁻¹) and 1765 cm⁻¹ (I = 717 km mol⁻¹).

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