THE IR SPECTRA OF CARBONYL OXIDE AND DIOXIRANE:
A THEORETICAL INVESTIGATION AT A CORRELATED LEVEL

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Harmonic frequencies, IR intensities and ^{18}O isotopic shifts for carbonyl oxide and dioxirane have been calculated at the MP2/6-31G* level of theory. The results are discussed with respect to an experimental distinction between the two peroxide isomers by low-temperature IR spectroscopy.

1. Introduction

Carbonyl oxide (1) has attracted considerable interest since it was first postulated as a reactive intermediate in the ozonolysis of alkenes by Criegee [1]. For more than 30 years its presence in ozonolysis reactions could only be substantiated indirectly, e.g. by its reaction with alcohols to yield alkoxyhydroperoxides [2]. However, recent developments in matrix isolation techniques have opened a new avenue for eventually detecting 1 directly. Oxidation of diazo compounds or carbenes [3] has already led to the direct observation of substituted 1 with the aid of low-temperature IR and UV spectroscopy [4]. Unfortunately these investigations are complicated by the fact that besides 1 several other oxygen-containing products are formed in the matrix, in particular the cyclic isomer of 1, dioxirane (2) [‡]. Since genuine spectra of 1 and 2 have not yet been reported, much of the spectroscopic work has to be based on assumptions. In this situation, theory can make a valuable contribution by providing data that lead to an unequivocal spectroscopic identification of labile compounds like 1, 2 or their derivatives.

In this spirit we have calculated the IR spectrum of both 1 and 2 employing ab initio molecular orbital theory. This work is part of a continuous effort aimed

at determining the properties of labile peroxides such as 1 or 2 by theoretical means [6–8].

2. Computational methods

Previous calculations on 1 and 2 have shown [6] that a reliable theoretical description of these molecules requires at least a split-valence basis set augmented by polarization functions and inclusion of electron correlation. Therefore, we have used throughout this work Pople's 6-31G* basis set [9] in conjunction with second-order Møller–Plesset perturbation theory (MP2) [10]. Equilibrium geometries of 1 and 2 at the MP2/6-31G* level of theory [6] are shown in fig. 1. Vibrational frequencies of the two peroxides have been calculated within the harmonic approximation by numerical differentiation of the analytic gradient [11]. IR intensities for the fundamental vibrational modes have been obtained by calculating the dipole moment derivatives numerically with respect to the Cartesian coordinates and transforming them to normal coordinates [12]. At the MP2 level of theory the dipole moment μ is given by the derivative of the energy with respect to the three components of a static electric field f [13],

$$\mu_i = -dE/df_i , \quad i = x, y, z .$$

The calculation of μ(MP2) requires the solution of the coupled perturbed Hartree–Fock (CPHF) equa-

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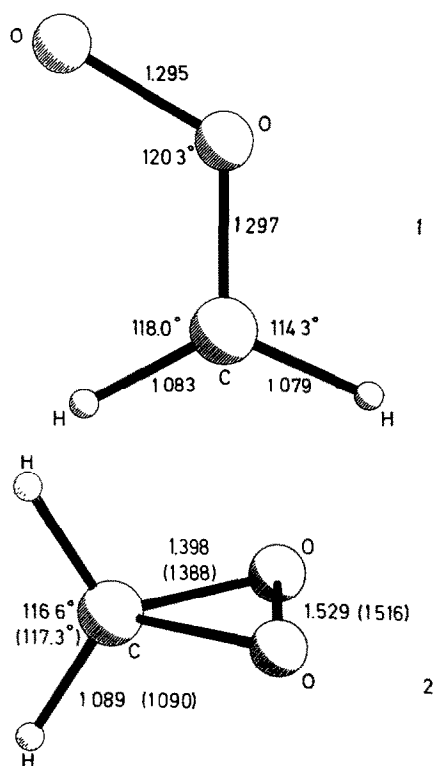[‡] 2 was first detected by microwave spectroscopy, see ref. [5].

Fig. 1. MP2/6-31G* geometries of carbonyl oxide (1) and dioxirane (2) [6]. The experimental geometry of 2 [5] is shown in parentheses. Bond lengths and bond angles are given in Å and deg, respectively.

tions [11] and involves similar considerations as for the computation of analytical gradients. MP2/6-31G* harmonic frequencies are known to exceed experimental frequencies by 5–10%. In order to account for this systematic deviation, all theoretical frequencies have been scaled by 0.93 [14] [‡].

Calculations have been carried out with a program package that contains large parts of GAUSSIAN 82 [16] and routines to determine the frequencies of

isotopomers and to calculate IR intensities at various levels of theory [17] [#].

3. Results and discussion

Calculated harmonic frequencies and IR intensities for 1 and 2 are listed in table 1. In fig. 2, the IR spectra derived from the data in table 1 are shown.

According to theory there is a large difference in the absolute intensities of the vibrational modes of 1 and 2. The two most intense absorptions of 1, ν_5 and ν_6, are 10–15 times stronger than the strongest IR bands of 2. This means that 1 should be easier to observe with the aid of IR spectroscopy than 2.

All vibrational modes of 1 that involve the three heavy atoms (ν_4, ν_5, ν_6 and ν_7, table 1) contain to some extent an admixture of CH_2 rocking. The most intense absorptions in the IR spectrum stem from the OO (ν_6) and CO (ν_5) stretching modes. Another mode, which should be typical of 1, is ν_4 (CH_2 rocking coupled with COO deformation, table 1), but its intensity is 7–13 times weaker than the intensity of ν_5 and ν_6. The fourth mode involving the three heavy atoms of 1, ν_7, corresponds to a COO deformation. Its intensity is so small (table 1) that observation of the corresponding band in the IR spectrum is doubtful. All other vibrational modes of 1 are due to motions of the CH_2 group. They are of little significance for the IR spectroscopic identification of 1 (compare with fig. 2).

Compared to typical OO stretching frequencies, e.g. that of H_2O_2 (exp.: 863 cm^{-1} [18], MP2/6-31G* (scaled): 864 cm^{-1} (ref. [14], see also footnote [‡]), ν_5 of 1 appears at a rather high frequency (1028 cm^{-1}, scaled value, table 1). This is indicative of the partial double bond character of the OO bond similar to that found for ozone (OO bond order: 1.5, experimental OO stretching frequencies: 1103 cm^{-1} (sym.) and 1042 cm^{-1} (asym.) [19]). In the case of the CO stretching frequency ν_5, the calculated value is only slightly larger than the values observed for CO single bonds (e.g. methanol, experimental CO stretching fre-

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[*] A more sophisticated scaling procedure, which accounts for the different description of stretching and deformation frequencies by the theoretical method used, has been proposed for example by Pulay et al. [15]. However, at the MP2/6-31G* level of theory the difference in the calculated frequencies is on average only 10–20 cm^{-1}, if both scaling methods are compared.

[#] C85 [17] contains routines for the analytical calculation of IR and Raman intensities at the HF level of theory and for the numerical computation of IR intensities at correlation corrected levels (MP2 and CISD).

Table 1
Harmonic vibrational frequencies for carbonyl oxide (1) and dioxirane (2) calculated at the MP2/6-31G* level

Symmetry	Mode	Type	Frequency [a] (cm^{-1})	Intensity (km/mol)
carbonyl oxide (1)				
A'	ν_1	CH str., asym.	3402 (3164)	1.1
	ν_2	CH str., sym.	3226 (3000)	13.3
	ν_3	CH$_2$ scissor	1498 (1393)	1.2
	ν_4	CH$_2$ rock, OOC def.	1314 (1222)	39.5
	ν_5	CO str.	1200 (1116)	291.6
	ν_6	OO str.	1105 (1028)	561.2
	ν_7	OOC def., CH$_2$ rock	561 (522)	6.7
A''	ν_8	CH$_2$ twist	786 (731)	30.7
	ν_9	CH$_2$ wag	664 (618)	42.3
dioxirane (2)				
A$_1$	ν_1	CH str., sym.	3154 (2933)	24.8
	ν_2	CH$_2$ scissor	1604 (1492)	5.0
	ν_3	CO str., sym.	1304 (1213)	28.5
	ν_4	OCO def., OO str.	789 (734)	2.2
A$_2$	ν_5	CH$_2$ twist	1033 (961)	0.0
B$_1$	ν_6	CH str., asym.	3260 (3032)	35.5
	ν_7	CH$_2$ rock	1208 (1123)	7.6
B$_2$	ν_8	CH$_2$ wag	1285 (1195)	0.2
	ν_9	CO str., asym.	955 (888)	23.9

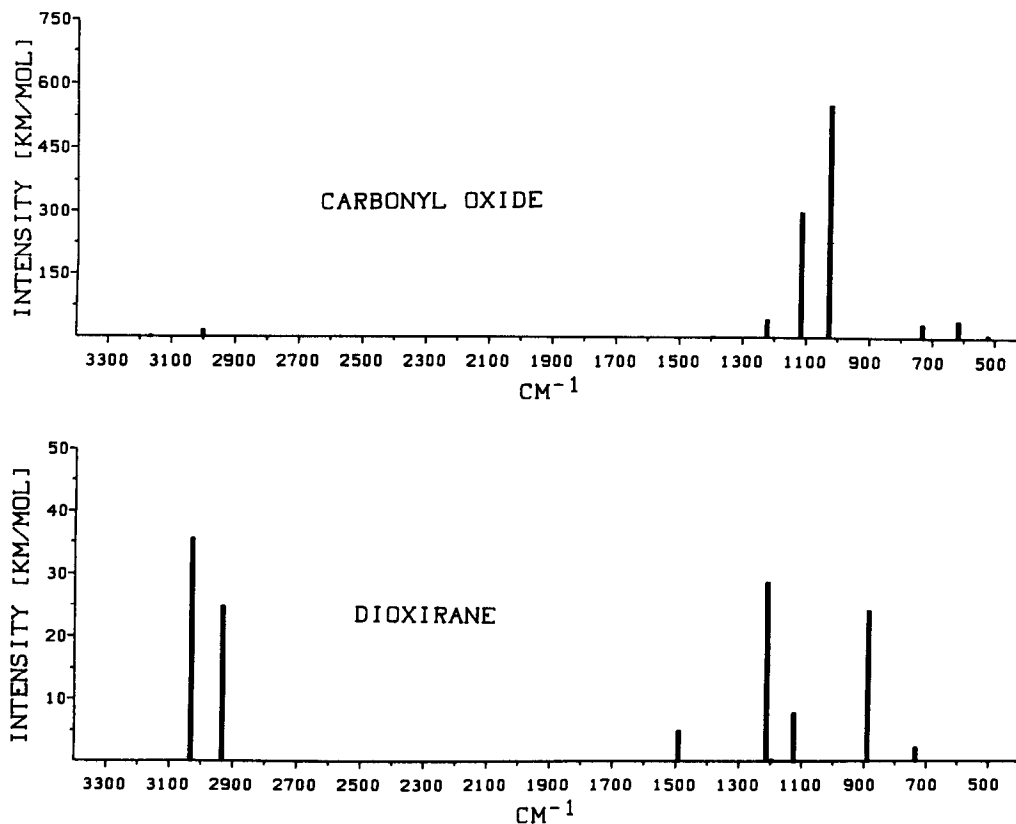[a] Frequencies scaled by a factor of 0.93 are given in parentheses.

Fig. 2. MP2/6-31G* IR spectra of carbonyl oxide (1) and dioxirane (2). Ab initio frequencies have been scaled by 0.93. Note that different scales for the intensities have been used.

Table 2
Calculated ^{18}O isotopic shifts in cm^{-1} for the MP2/6-31G* vibrational frequencies of carbonyl oxide (1) and dioxirane (2)

Frequency [a]	Carbonyl oxide (1)			Dioxirane (2)	
	$H_2{}^{12}C^{16}O^{18}O$	$H_2{}^{12}C^{18}O^{16}O$	$H_2{}^{12}C^{18}O^{18}O$	$H_2{}^{12}C^{16}O^{18}O$	$H_2{}^{12}C^{18}O^{18}O$
ν_1	0	0	0	0	0
ν_2	0	0	0	0	−1
ν_3	−2	−3	−5	−16	−32
ν_4	−7	−25	−32	−19	−39
ν_5	0	−20	−22	−2	−5
ν_6	−29	−20	−49	0	0
ν_7	−9	−9	−18	−1	−3
ν_8	−2	−6	−7	0	1
ν_9	−1	−2	−3	−17	−34

[a] For the symmetry and type of frequency see table 1.

quency: 1029 cm^{-1} [18]). Such a comparison, however, is complicated by the fact that both OO and CO stretching modes couple with the CH_2 rocking mode. If substituted 1 is investigated by IR spectroscopy, this coupling may change the vibrational spectrum significantly [20].

Upon isotopic substitution by ^{18}O, the modes ν_4, ν_5, ν_6 and ν_7 of 1 all undergo relatively large shifts (table 2), which should be very helpful with regard to an IR spectroscopic identification. The largest shifts are calculated for ν_4 and ν_6 (−32 and −49 cm^{-1}, table 2). If only one of the two oxygens of 1 is replaced by ^{18}O, two isotopomers with different isotopic shifts result. Note the difference in the shift of ν_5 (zero for $H_2C^{16}O^{18}O$ and −20 cm^{-1} for $H_2C^{18}O^{16}O$, table 2). This supports our characterization of ν_5 as a CO stretching mode. This distinction may be useful, if e.g. 1 is prepared by oxidation of carbene with $^{16}O^{18}O$ [4]. The "splitting" of vibrational frequencies ν_4, ν_5 and ν_6 (table 2) will facilitate the identification of 1.

The IR spectrum of 2 (fig. 2) is characterized by the CO stretching modes ν_3 (sym., 1213 cm^{-1}) and ν_9 (asym., 888 cm^{-1}, table 1), which are of comparable intensity. The third mode that is due to motions of the three heavy atoms, ν_4, appears at 734 cm^{-1} (OCO deformation, OO stretching) but its low intensity will probably hinder its observation in the IR spectrum. All other modes correspond to motions of the CH_2 group [‡]. The frequency of the OO stretching mode of 2 is 130 cm^{-1} lower than that of H_2O_2, which is in line with the weakening of the OO bond

in 2 (2: $R(OO)$ = 1.529 Å, fig. 1; H_2O_2: $R(OO)$ = 1.456 Å [22]. The CO stretching frequencies are similar to those observed for oxirane (sym. 1266 cm^{-1}, asym. 892 cm^{-1} [18]). ^{18}O substitution affects the three modes by 16–39 cm^{-1} (table 2) where the smaller shifts are due to single substitution.

We *conclude* that

(1) the IR spectra of 1 and 2 should be easily distinguishable from the large differences in the intensities of the strongest bands (fig. 2);

(2) the IR spectrum of 1 is characterized by two very strong absorptions at 1116 and 1028 cm^{-1} that will vanish if 1 decomposes or rearranges to 2;

(3) the presence of 2 is best recognized by an absorption at 888 cm^{-1}; the absorption at 1213 cm^{-1} probably overlaps with a band from 1 (ν_4) possessing a similar intensity;

(4) the heavy atom modes of 1 couple with those of the CH_2 group more than the heavy atom modes of 2; this may be of importance if substituted 1 or 2 is investigated by IR spectroscopy;

(5) relatively large isotopic shifts can be expected for 1 and 2; of these only $\Delta\nu_5$ (1) at 1116 cm^{-1}, $\Delta\nu_6$(1) at 1028 cm^{-1} and $\Delta\nu_9$(2) at 888 cm^{-1} will be of experimental relevance;

(6) single substitution of ^{16}O by ^{18}O leads to a splitting of vibrational frequencies ν_4, ν_5, and ν_6 for 1; the splitting for ν_5 (1116 cm^{-1}) should be the · most characteristic.

[‡] A previous calculation of the IR spectrum of 2 at the HF level by Francisco and Williams [20] is erroneous with regard to the calculated intensities.

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