Dioxirane vibrational frequencies: an unsettling relationship between theory and experiment

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There appears to be a conflict between theory and experiment concerning the vibrational frequencies of dioxirane, a CH_2O_2 isomer. Here we employ sophisticated *ab initio* quantum mechanical methods with large basis sets to determine geometry, harmonic vibrational frequencies, infrared (IR) intensities and isotopic shifts of dioxirane. At the highest level of theory, the CCSD(T) approach is used together with a cc-VTZ2P+f,d basis set. Best predictions for CO asymmetric and OO stretching (or OCO deformation) harmonic frequencies are 931 (b_2) cm^{-1} and 759 (a_1) cm^{-1}, respectively. The IR intensities of these two peaks are predicted to be 19 km mol^{-1} and 1 km mol^{-1}. An examination of the experimental vibrational frequencies of substituted dioxiranes is also presented. Calculated frequencies, intensities, and isotopic shifts all imply that the two experimental IR features (with their observed intensity ratio of 2·8) assigned to CO stretching (839·0 cm^{-1}) and OCO deformation (800·9 cm^{-1}) frequencies by J. R. Sodeau and L. J. Whyte (1991, *J. chem. Soc. Faraday Trans.*, **87**, 3725) should be re-addressed.

1. Introduction

Since the reaction mechanism between ethylene and ozone was proposed by Criegee [1] in 1949, carbonyl oxides, CR_2OO, have attracted a great deal of attention as important intermediates of the ozonolysis reaction [2, 3], along with ozone van der Waals complexes [4, 5] and five-membered ring intermediates such as primary [6–9] and secondary ozonides [10, 11]. Because of its instability, carbonyl oxide, CH_2OO, itself has not been observed directly, even though there is sufficient indirect evidence for the involvement of this intermediate in the ozonolysis of ethylene and substituted ethylenes [2, 3]. Information on the electronic structure of CH_2OO comes exclusively from *ab initio* calculations [12–20] while the nature of the molecule in condensed phases (diradical or zwitterionic) is still an open question [2, 3].

Difficulties in identifying CH_2OO are caused by the high reactivity of the molecule. In the presence of aldehydes and ketones, carbonyl oxide most probably exists only in the form of a dipole complex [21] that rearranges with a low barrier to more stable species; with nucleophilic (N) or electrophilic reaction partners (E) it reacts rapidly to yield compounds of the general form NCH_2OOE (e.g., N–E = RO–H) while in the

absence of any suitable reaction partner rapid isomerization to its cyclic form, dioxirane, is most likely [2, 3].

Dioxirane, which is known as a powerful oxygen transfer reagent, was detected experimentally first in the reaction between ethylene and ozone by Lovas and Suenram in 1977 [22] who determined the r_s geometry of the molecule by microwave spectroscopy. Subsequently, extensive investigations by both experiment [23–25] and theory [14, 15, 20] have been carried out to characterize this compound spectroscopically. The energy separation between carbonyl oxide and dioxirane has been reported to be 26 kcal mol^{-1}, while the barrier for cyclization has been predicted to be 19 kcal mol^{-1} in a recent theoretical paper [20].

The experimental observation of fundamental vibrational frequencies for dioxirane was not reported until 1991, when Sodeau and Whyte obtained a FTIR spectrum from the matrix photolysis of CH_3I in the presence of molecular oxygen and tentatively assigned it to dioxirane [25]. Their experimental frequencies of 839·0 cm^{-1} and 800·9 cm^{-1}, which were assigned to CO and OO stretching modes, respectively, seem to be in plausible agreement with the early theoretical predictions (scaled SCF/3-21G(d) result of 803 cm^{-1} and 765 cm^{-1}) of Francisco and Williams [14]. However, more recent theoretical predictions for these frequencies are not consistent with the experimental results. Specifically, Gauss and Cremer [15] predicted the CO and OO stretching frequencies to be 888 cm^{-1} and 734 cm^{-1} at the MP2/6-31G(d) level of theory in 1988. Similarly, Cremer, Gauss, Kraka, Stanton and Bartlett [20] predicted for the same frequencies 932 cm^{-1} and 701 cm^{-1} at the CCSD(T)/DZP level in 1993. Because of the difference between theoretical and measured CO and OO stretching frequencies, Sodeau and Whyte state: ''This work does not appear to support the higher-level *ab initio* calculations; clearly the theoretical work needs to be re-addressed'' [25].

The need for a reinvestigation of the dioxirane spectrum is also given by the fact that state of the art calculations by Cremer and coworkers (CCSD(T)/TZ2P) led to an OO bond length of dioxirane that compared with the r_s value of the microwave study (1·516 Å) [22] is too long by 0·016 Å, which cannot be explained by the typical deviations between r_s and r_e and, accordingly, suggests deficiencies in either the experimental or computational determination of the geometry of dioxirane. In the latter case, errors in the calculation of the IR spectrum, in particular the OO and CO stretching frequencies, are likely which might have added to the difficulties in identifying dioxirane in the matrix FTIR experiment of Sodeau and Whyte [25].

In the present paper we report geometrical parameters, rotational constants, dipole moment, harmonic vibrational frequencies, IR intensities and isotopic frequency shifts for dioxirane predicted at a high level of theory using large basis sets including an extensive treatment of electron correlation. We demonstrate the importance of using f-type polarization functions in the *ab initio* description of dioxirane, which was not considered in any of the previous investigations of this molecule [12–20]. Based on the frequencies, IR intensities and isotopic shifts calculated at the CCSD(T) level with a large basis set including f functions, we assign all bands of the IR spectrum of dioxirane and compare them with the fundamental frequencies observed and tentatively assigned by Sodeau and Whyte [25].

2. Theoretical approach

The basis sets used in this study are of double zeta plus polarization (DZP), triple zeta plus double polarization (TZ2P), and TZ2P+f,d quality. The DZP basis set is the standard Huzinaga [26] and Dunning [27] double zeta (DZ) (9s5p/4s2p) contracted Gaussian basis set for carbon and oxygen and the (4s/2s) set for hydrogen plus a single set of Cartesian polarization functions (d functions on C and O, and p functions on hydrogen) with orbital exponents $\alpha_d(C) = 0.75$, $\alpha_d(O) = 0.85$, and $\alpha_p(H) = 0.75$. The second basis, TZ2P, is of triple zeta (TZ) quality with two sets of Cartesian polarization functions with exponents $\alpha_d(C) = 1.5, 0.375$, $\alpha_d(O) = 1.7, 0.425$, and $\alpha_p(H) = 1.5, 0.375$. The TZ basis consists of the Huzinaga [26] and Dunning [28] (10s6p/5s3p) set for C and O, and the (5s/3s) set for H. The TZ2P+f,d basis set used is the TZ2P basis augmented with sets of spherical f functions on C and O with exponents $\alpha_f(C) = 0.8$, $\alpha_f(O) = 1.40$, and a set of d functions on H with $\alpha_d(H) = 1.0$. Since CCSD(T) calculations with this basis were not feasible, we employed for our final calculations a slightly smaller and more contracted VTZ basis that is augmented by spherical rather than Cartesian polarisation functions (five d and seven f). The VTZ basis set we used is Dunning's correlation corrected (cc)-VTZ2P basis, which is composed of a (10s5p2d/4s3p2d) contraction for C and O and a (5s2p1d/3s2p1d) contraction for H [29]. The exponents of the polarization functions of the cc-VTZ2P set and the corresponding cc-VTZ2P+f,d basis set (C and O : 1·097, 0·318(d), 0·761(f) ; 2·314, 0·645(d), 1·428(f) ; H : 1·407, 0·388(p), 1·057(d)) have been optimized consistently in correlation calculations of the CISD type [29]. In total, five different basis sets (DZP, TZ2P, cc-VTZ2P, TZ2P+f,d, cc-VTZ2P+f,d) of increasing size and flexibility were used.

The geometry of dioxirane was fully optimized at the self-consistent field (SCF) level of theory using analytical gradient techniques [30] with DZP, TZ2P, and TZ2P+f,d basis sets. The SCF equilibrium geometries were used subsequently for optimizations at the single and double excited configuration interaction (CISD) level with the DZP, TZ2P, and TZ2P+f,d basis sets by employing analytical CISD gradient methods [31]. The CISD energies were corrected for unlinked quadruple excitations by using Davidson's method and corrected CISD results are denoted by CISD+Q [32]. The CISD/DZP and CISD/TZ2P geometries were finally used to obtain geometries optimized at the CCSD and CCSD(T) levels, which are the single and double excitation coupled cluster method and CCSD with the effects of connected triple excitations included perturbatively [33, 34]. CCSD and CCSD(T) optimized geometries were obtained employing both DZP, TZ2P, and TZ2P+f basis sets. In the CISD, CCSD, and CCSD(T) wavefunctions, the three core-like occupied SCF molecular orbitals were frozen (held doubly occupied) and the three highest virtual molecular orbitals were deleted from the correlation procedures. The latter constraint was released when determining the final set of geometrical parameters at CCSD(T) with the cc-VTZ2P+f,d basis. Results thus obtained are denoted by CCSD(T)(full)/cc-VTZ2P+f,d.

Harmonic vibrational frequencies and infrared intensities of dioxirane were evaluated using analytical second energy derivatives [35] at the SCF level and using finite displacements of analytical gradients at the CISD, CCSD, and CCSD(T) levels of theory. The majority of computations described above were carried out with the PSI-2 [36] suite of computer programs.

3.   Results and discussion

The predicted geometry for the ground state of dioxirane at the highest level of theory (CCSD(T)(full)/cc-VTZ2P+f,d) is presented and compared with experiment [22] in figure 1. The absolute energies and the geometrical parameters at other levels of theory are listed in table 1. In general, bond lengths decrease with increasing basis set size, while electron correlation increases the bond distances. An exception to this trend is found for the OO bond length (table 1), which increases very slightly with basis set change from DZP to TZ2P at the SCF, CCSD, and CCSD(T) levels. Bond angles are largely stable with respect to both electron correlation and basis set size. In general, for the dioxirane geometry, the effects of increasing the basis set from DZP to TZ2P are not very significant at correlated levels of theory such as CISD, CCSD, and CCSD(T). The CCSD(T) geometries obtained in this work confirm the CCSD(T) results of Cremer and co-workers [20], i.e., they suggest an OO bond length which is 0·02–0·03 Å longer than the corresponding experimental value.

However, when adding f-type polarization functions to the TZ2P basis for C and O a significant reduction in the lengths of the CO and OO bonds is obtained. The magnitude of this reduction increases as higher level correlation effects are covered by the method used. The CO bond lengths are shortened by about 0·009 Å and the OO bond length by about 0·020 Å while the CH bond lengths are slightly increased (0·002–0·005 Å, table 1), obviously as a result of a transfer of electron density from the CH bond regions to the OO and CO bond regions. The best description of the dioxirane geometry is obtained at the CCSD(T)(full)/cc-VTZ2P+f,d level of theory, which leads to OO and CO bond lengths of 1·514 Å and 1·385 Å, in excellent agreement with the experimental r_s values of 1·516(3) Å and 1·388(4) Å, respectively.

Calculated and experimental rotational constants and dipole moment of dioxirane are compared in table 2. One could expect that, parallel to the improved description of the geometry due to the addition of f functions, there is a similar improvement of the calculated rotational constants. However, only the rotational constant B is improved by the use of f functions, while the constants A and C deviate somewhat more from experimental values than the corresponding cc-VTZ2P values (table 2). This reflects the fact that the CH bond lengths of our final CCSD(T) geometry (figure 1, table 1) are 0·007 Å shorter than the experimental r_s values (1·090(2) Å [22]). At the CCSD(T)/TZ2P+f,d level, the calculated CH bond lengths are predicted to be 1·087 Å (table 1) and the rotational constants clearly are in better agreement with experimental values (table 2) despite a calculated OO bond length which is 0·007 Å too long (table 1). Clearly, a correct description of the OO bond is more important for the discussion of the IR spectrum of dioxirane below 2000 cm^{-1}. It is also interesting to note that both theory and experiment suggest a CH bond length of 1·080 Å in the case of cyclopropane [37], and that a CH bond length of 1·090 Å for dioxirane seems to be rather long.

The inclusion of f functions leads to only a slight improvement in the dipole moment from 2·53 D to 2·51 D compared with an experimental value of 2·48(7) D [22] (D = debye ≈ 3·335 64 × 10^{-3} C m). The relatively large f function effects on the calculated CO and OO bond lengths imply that the vibrational frequencies of the CO and OO stretching modes might vary significantly when extending the basis set by f functions. On the other hand, the small sensitivity of the molecular dipole moment with regard to f polarization functions suggests that calculated IR intensities might change only slightly when replacing a TZ2P by TZ2P+f,d basis.
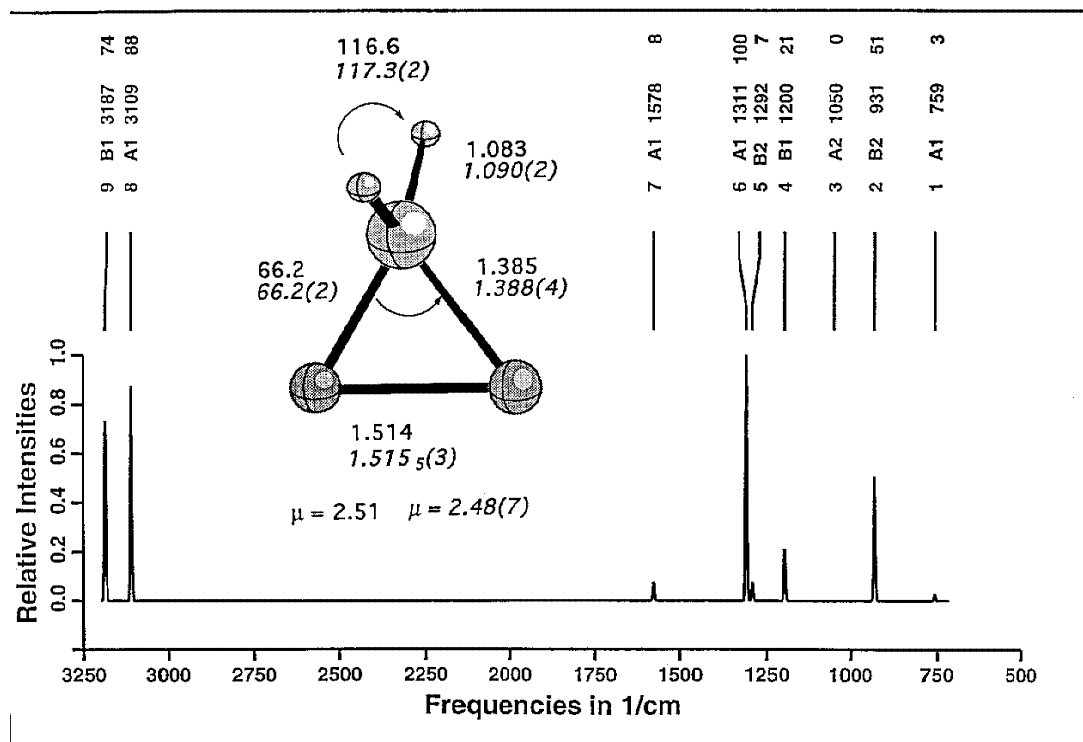
Figure 1. CCSD(T)(full)/cc-VTZ2P+f,d infrared spectrum of dioxirane. For the assignment of IR bands and absolute intensities, see table 3. In the insert, the CCSD(T)(full)/cc-VTZ2P+f,d equilibrium geometry is compared with the r_s geometry (numbers in italics) of the MW investigation of Suenram and Lovas [22]. Bond lengths in Å, angles in deg; uncertainties of the r_s values [22] in parentheses.

Harmonic vibrational frequencies and IR intensities of dioxirane at various levels of theory are presented in table 3. There is one IR inactive a_2 mode among the total of nine vibrational frequencies for dioxirane (C_{2v} symmetry, see figure 1). The first and only measurement of the IR spectrum for dioxirane was reported with the tentative assignments for the CO asymmetric stretching (839 cm^{-1}) and OCO deformation (800·9 cm^{-1}) frequencies by Sodeau and Whyte in 1991 [25]. Their experimental values are in plausible agreement with the early low level (SCF/3-21G(d)) theoretical predictions of 803 cm^{-1} and 765 cm^{-1}, respectively, by Francisco and Williams in 1985 [14]. However, there are discrepancies between the above experimental observations and higher level predictions of 888 cm^{-1} and 734 cm^{-1} at the MP2/6-31G(d) level by Gauss and Cremer in 1987 [15], and of 932 cm^{-1} and 701 cm^{-1} at the CCSD(T)/DZP level of theory by Cremer and coworkers in 1993 [20]. For the relative intensities (CO stretch/OCO deformation), the situation is similar to the case of the vibrational frequencies, i.e., the relative intensity is 2·8 for the two observed bands and appears to be in good agreement with the early low-level prediction of 2·6. However, the experimental ratio is inconsistent with the result at higher levels of theory which are predicted to be 10·9 at MP2/6-31G(d) [15] and 39·2 at CCSD(T)/DZP [20].

In the present study harmonic vibrational frequencies have been evaluated using an extensive treatment of electron correlation and an extended basis set (TZ2P) for the highest level methods. In addition, the effects of f functions are considered at the CISD (TZ2P+f,d) and CCSD(T) levels of theory (cc-VTZ2P+f,d). At both the SCF and CISD level of theory, the effects of f functions are relatively large for the vibrational frequencies affected by the CO and OO bonds, such as the CO symmetric and

Table 1.   Absolute energies and geometrical parameters of dioxirane (CH_2O_2) at various levels of theory.[a]

Method/basis set	Energy	R(CH)	R(CO)	R(OO)	θ(HCH)
SCF/DZP	−188·654854	1·081	1·361	1·441	116·5
SCF/TZ2P	−188·678716	1·075	1·358	1·444	116·6
SCF/TZ2P+f,d	−188·687856	1·077	1·353	1·434	116·3
CISD/DZP	−189·109765 (−189·163795)[b]	1·088	1·382	1·486	116·6
CISD/TZ2P	−189·200244 (−189·262364)[b]	1·077	1·377	1·484	116·8
CISD/TZ2P+f,d	−189·261848 (−189·329840)[b]	1·078	1·368	1·465	116·6
CCSD/DZP	−189·166692	1·094	1·395	1·517	116·5
CCSD/TZ2P	−189·267679	1·083	1·391	1·519	116·8
CCSD/TZ2P+f,d	−189·334382	1·085	1·382	1·497	116·6
CCSD(T)/DZP	−189·183962	1·096	1·400	1·540	116·4
CCSD(T)/TZ2P	−189·294390	1·085	1·399	1·547	116·8
CCSD(T)/TZ2P+f,d	−189·363822	1·087	1·390	1·523	116·7
CCSD(T)(full)/cc-VTZ2P	−189·334324	1·082	1·394	1·532	117·0
CCSD(T)(full)/cc-VTZ2P+f,d	−189·399045	1·083	1·385	1·514	116·8

[a] Frozen core calculations (except where noted otherwise): energies in E_h (E_h = hartree $\approx 4.359 \times 10^{-18}$ J); bond lengths in Å; bond angles in deg.
[b] Davidson corrected CISD energies, CISD+Q, in parentheses.

Table 2. Calculated and experimental dipole moments and rotational constants of dioxirane.[a]

Method/basis	μ	A	B	C	σ
CCSD(T)(full)/cc-VTZ2P	2·53	29·049	24·670	14·667	0·191
CCSD(T)(full)/cc-VTZ2P+f,d	2·51	29·216	25·227	14·905	0·179
CCSD(T)/VTZ2P+f,d		29·058	24·925	14·770	0·074
Exp.[b]	2·48(7)	28·976	25·056	14·780	—

[a] Dipole moments in D; rotational constants A, B, and C in GHz; σ denotes the mean deviation between experimental and calculated rotational constants.
[b] From reference [22].

asymmetric stretching and the OO stretching frequencies. This result can be understood from the significant changes in geometrical parameters with the addition of f functions. The consistent changes of geometrical parameters upon adding f functions at the correlated levels of theory (table 1) explain why the effect of f functions on the vibrational frequencies is also consistent from CISD to CCSD(T).

The CCSD(T)(full)/cc-VTZ2P+f,d harmonic vibrational frequency for the OCO deformation (or OO stretching) is 759 cm^{-1} and for the CO stretching modes 931 cm^{-1} (asymmetric) and 1311 cm^{-1} (symmetric). These values can be compared with experimental results for some substituted dioxiranes listed in table 4 [38, 40–42]. For example, for dimethyldioxirane, Murray and Jeyaraman [38] report IR frequencies of 784, 899 and 1209 cm^{-1}, which we relate to the OO and CO stretching modes. According to calculations carried out by Cremer and Schindler [39], the methyl substituents lead to a strengthening of the OO and a weakening of the CO bonds, which means that the associated dimethyldioxirane stretching frequencies represent upper and lower bounds to the corresponding dioxirane frequencies. We note that the CCSD(T)(full)/cc-VTZ2P+f,d frequencies are in line with this, whereas in the case of the experimental frequency values reported by Sodeau and Whyte (801 cm^{-1} and 839 cm^{-1}) [25] this is not true.

For difluorodioxirane, Russo and DesMarteau measured the following three-membered ring frequencies: 511 cm^{-1} (vw, a_1, OCO deformation, OO stretching), 911 cm^{-1} (m, b_2, asymmetrical CO stretching), and 1464 cm^{-1} (vs, a_1, symmetrical CO stretching) [42]. MP2 and MP4 calculations reveal that F substituents lead to significant weakening of the OO bond and strengthening of the CO bonds [43], which is reflected nicely by the measured a_1 stretching frequencies of difluorodioxirane. Because of the pronounced changes in geometry due to F,F substitution, it is not possible to draw any conclusions with regard to the fundamental frequencies of the parent molecule. Therefore, it may be just accidental that the asymmetric CO stretching frequency of the difluorodioxirane is within 20 cm^{-1} of the value we predict for the corresponding mode of the parent molecule.
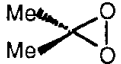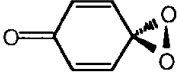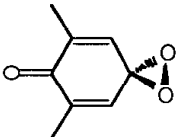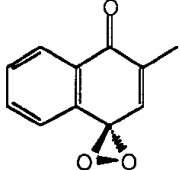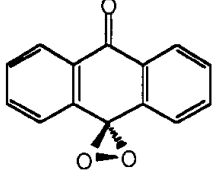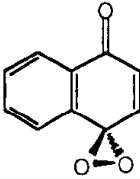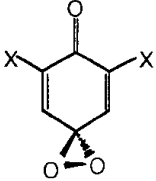
The isomeric dioxiranes of the *p*-benzoquinone *O*-oxides listed in table 4 have been investigated by Sander and coworkers [40, 41]. The largest isotopic shifts due to $^{18}O\,^{18}O$ incorporation are observed for the frequencies given, suggesting that they can be associated in the order of increasing magnitude with OO and CO stretching modes. In some cases, all three frequencies could not be observed because of vanishing intensities or overlapping bands of other origin [40, 41]. Assigned OO stretching frequencies are in a remarkably good agreement with the corresponding CCSD(T)(full)/cc-VTZ2P+f,d value (759 cm^{-1}, table 4) while the CO stretching

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Table 3. Harmonic vibrational frequencies (in cm^{-1}) and IR intensities (in km mol^{-1}) for dioxirane at various levels of theory.[a]

Method/basis	$\omega_1(b_1)$ CH asym. str.	$\omega_2(a_1)$ CH sym str.	$\omega_3(a_1)$ CH$_2$ scissor	$\omega_4(a_1)$ CO sym str.	$\omega_5(b_2)$ CH$_2$ wag	$\omega_6(b_1)$ CH$_2$ rock	$\omega_7(a_2)$ CH$_2$ twist	$\omega_8(b_2)$ CO asym. str.	$\omega_9(a_1)$ OO str.
SCF/DZP	3374(35)	3276(51)	1693(16)	1485(71)	1387(3)	1278(13)	1141(0)	997(36)	958(2)
SCF/TZ2P	3358(27)	3262(41)	1689(7)	1458(70)	1404(4)	1284(13)	1150(0)	965(34)	945(2)
SCF/TZ2P+f,d	3338(30)	3243(42)	1690(9)	1473(71)	1405(3)	1285(13)	1151(0)	984(36)	961(2)
CISD/DZP	3311(46)	3208(44)	1625(10)	1394(47)	1318(8)	1222(67)	1069(0)	976(16)	863(1)
CISD/TZ2P	3299(33)	3207(34)	1616(4)	1367(50)	1336(6)	1217(63)	1088(0)	940(17)	853(2)
CISD/TZ2P+f,d	3296(32)	3196(32)	1623(5)	1401(52)	1337(6)	1232(63)	1092(0)	974(18)	884(2)
CCSD/DZP	3235(49)	3134(44)	1586(8)	1329(39)	1281(8)	1192(62)	1033(0)	943(13)	782(1)
CCSD/TZ2P	3213(35)	3124(34)	1571(3)	1296(41)	1294(5)	1181(58)	1050(0)	903(13)	770(1)
CCSD(T)/DZP	3211(52)	3110(47)	1572(7)	1294(36)	1266(7)	1181(60)	1018(0)	921(11)	721(1)
CCSD(T)/TZ2P	3184(38)	3096(36)	1552(2)	1250(38)	1275(4)	1164(55)	1031(0)	876(11)	702(1)
CCSD(T)(full)/ cc-VTZ2P	3177(29)	3090(34)	1567(3)	1277(37)	1293(2)	1194(8)	1048(0)	902(18)	732(1)
CCSD(T)(full)/ cc-VTZ2P+f,d	3187(28)	3109(34)	1578(3)	1311(38)	1292(3)	1200(8)	1050(0)	931(19)	759(1)

[a] Intensities are given in parentheses.

Table 4. Comparison of calculated and assumed OO and CO stretching frequencies for dioxirane with measured frequencies of substituted dioxiranes: all frequencies in cm^{-1}; relative intensities in parentheses.

Molecule	OO stretch	CO stretch, asym	CO stretch, sym	Ref.
(dioxirane, O—O)	759 (1)	931 (19)	1311 (38)	this work
	801 (1)	839 (3)		25
(dimethyldioxirane, Me, Me)	784	899	1209	38
(difluorodioxirane, F, F)	511 (vw)	911 (m)	1464 (s)	42
(quinone dioxirane)	750	889	1263	40,41
(dimethyl quinone dioxirane)	754		1357	40,41
(methylnaphthalenone dioxirane)	757		1317	40,41
(anthracenone dioxirane)	756			40,41
(naphthalenone dioxirane)	759 (1)	872	1273	40,41
X = Cl	732	884	1345	40,41
X = Br	861	1342		40,41

frequencies are 30–100 cm^{-1} smaller than the calculated dioxirane values. Again, a lengthening of the CO bonds in the substituted dioxiranes seems to be responsible for these trends.

The CCSD(T)(full)/cc-VTZ2P+f,d intensity of the CO asymmetric stretching band is 19 times larger than that of the OO stretching band, which is in reasonable

Table 5. CCSD(T)(full) and experimental ^{18}O isotopic shifts for the vibrational frequencies of dioxirane.[a]

Mode	cc-VTZ2P		cc-VT2P+f,d		Exp.
	$^{16}O\,^{18}O$	$^{18}O\,^{18}O$	$^{16}O\,^{18}O$	$^{18}O\,^{18}O$	$^{18}O\,^{18}O$
ω_1	0·2	0·2	0·2	0·1	
ω_2	0·2	0·3	0·3	0·3	
ω_3	0·4	0·6	0·3	0·3	
ω_4	15·4	31·6	19·6	32·1	
ω_5	0·5	1·0	3·5	1·0	
ω_6	1·3	2·7	1·3	2·7	
ω_7	2·6	5·0	2·6	5·1	
ω_8	16·3	31·4	16·8	32·5	43·8
ω_9	18·0	36·3	18·7	37·8	39·1

[a] Isotopic shifts in cm^{-1}; experimental values from [25].

agreement with some but not all experimental observations made for substituted dioxiranes [38, 40–42]. In passing on we note that in the dioxiranes of *p*-benzoquinone *O*-oxides, the OCO deformation (OO stretching) mode couples with C_RCC_R bending motions (C_R: substituent carbon), which can cause a redistribution of electron density and an increase in the IR intensity. Therefore, measured intensities of substituted dioxiranes may differ considerably from those of the OO and CO stretching modes of dioxirane. In any case, the CCSD(T)(full)/cc-VTZ2P+f,d intensity ratio of asymmetric CO and OO stretching bands differs strongly from the intensity ratio (2·8) measured by Sodeau and Whyte [25].

In table 5, calculated isotopic shifts of dioxirane are compared. For $^{18}O\,^{18}O$ substitution, the largest isotopic shift (38 cm^{-1}, table 5) is calculated for the OO stretching mode while the isotopic shifts for the CO stretching modes (32 cm^{-1}) are 6 cm^{-1} smaller, which is in line with the data published by Cremer and coworkers [20]. It seems that the extension of the basis set from DZP to TZ2P or TZ2P+f,d affects the isotopic shifts by just 1–2 cm^{-1} keeping relative isotopic shifts about constant. None of the high level calculations supports the assignment of a larger isotopic shift to the asymmetric CO stretching mode rather than the OO stretching mode as suggested by Sodeau and Whyte (44 cm^{-1} for asymmetric CO stretching; 39 cm^{-1} for OO stretching) [25].

The CO symmetric stretching frequency decreases significantly with the extension of the basis set from DZP to TZ2P and increases again with the addition of f functions. The CCSD(T)(full)/cc-VTZ2P+f,d value for this harmonic frequency is 1311 cm^{-1}, with an intensity (38 km mol^{-1}) about half of the IR intensity (71 km mol^{-1}) at the SCF level. The vibrational frequency of the CH_2 rocking mode is calculated to be 1200 cm^{-1}. Its intensity first increases, but then decreases with the improvement of the method (SCF/TZ2P+f,d: 13 km mol^{-1}; CCSD(T)/TZ2P: 55 km mol^{-1}; CCSD(T)(full)/cc-VTZ2P and CCSD(T)(full)/cc-VTZ2P+f,d: 8 km mol^{-1}), while the intensity of the CO asymmetric stretching mode decreases from 36 via 11 to 19 km mol^{-1} (table 3). The IR spectrum of dioxirane below 2000 cm^{-1} can be characterized (see figure 1) by two strong absorptions at 1311 cm^{-1} (CO sym. stretch) and at 931 cm^{-1} (CO asym. stretch) and by a less intense peak at 1200 cm^{-1} (CH_2 rock). The other four vibrational frequencies of dioxirane below 2000 cm^{-1} are not affected

significantly by the addition of f functions (except the OO stretch as described above), and their IR intensities are relatively weak.

4. Conclusion

The harmonic vibrational frequencies and IR intensities of dioxirane have been evaluated from equilibrium geometries optimized fully at the corresponding levels of theory using sophisticated *ab initio* quantum mechanical methods. The geometrical parameters predicted at the CCSD(T)(full)/cc-VTZ2P+f,d level are in excellent agreement with the experimental structure of Lovas and Suenram [22]. The effects of f functions on CO and OO bond distances are significant at the correlated levels of theory, implying that the considerations of f function effects are important for predicting precisely the vibrational frequencies for CO and OO stretching modes of dioxirane or substituted dioxiranes.

Considering (a) the CCSD(T)(full)/cc-VTZ2P+f,d values for the OCO deformation (OO stretching) and CO asymmetric stretching vibrational frequencies of dioxirane (759 cm^{-1} and 931 cm^{-1}) obtained in this work, (b) the OO and CO stretching frequencies of substituted dioxiranes (table 4), (c) the calculated IR intensities (1 km mol^{-1} and 19 km mol^{-1}), and (d) the calculated isotopic shifts ratios ($\Delta\omega_9$(OO) = 38 cm^{-1}; $\Delta\omega_8$(CO) = 32 cm^{-1}; $\Delta\omega_9$(OO)/$\Delta\omega_8$(CO) > 1), it becomes clear that the experimental features (at 801 cm^{-1} and 839 cm^{-1}; relative intensities: 1 and 2·8; $\Delta\omega$(801) = 39 cm^{-1}; $\Delta\omega$(839) = 44 cm^{-1}; $\Delta\omega$(801)/$\Delta\omega$(839) < 1) assigned tentatively to the OO and CO stretching frequencies of dioxirane by Sodeau and Whyte [25] arise from another source or sources.

The spectroscopic data presented in this work should be used to reexamine the IR spectrum of matrix isolated dioxirane.

References

[1] CRIEGEE, R., and WENNER, G., 1949, *Justus Liebiegs Ann. Chem.*, **564**, 9.
[2] SANDER, W., 1990, *Angew, Chem. Int. Edn Engl.*, **29**, 344.
[3] BUNNELLE, W. H., 1991, *Chem. Rev.*, **91**, 335; and references therein.
[4] GILLIES, C. W., GILLIES, J. Z., SUENRAM, R. D., LOVAS, F. J., KRAKA, E., and CREMER, D. 1991, *J. Amer. chem. Soc.*, **113**, 2412.
[5] GILLIES, J. Z., GILLIES, C. W., LOVAS, F. J., MATSUMURA, K., SUENRAM, R. D., KRAKA, E., and CREMER, D., 1991, *J. Amer. chem. Soc.*, **113**, 6408.
[6] HULL, L. A., HISATSUNE, I. C., and HEICKLEN, J., 1972, *J. Amer. chem. Soc.*, **94**, 4856.
[7] CREMER, D., 1979, *J. chem. Phys.*, **70**, 1898, 1911.
[8] KOHLMILLER, C. K., and ANDREWS, L., 1981, *J. Amer. chem. Soc.*, **103**, 2578.
[9] GILLIES, J. Z., GILLIES, C. W., SUENRAM, R. D., and LOVAS, F. J., 1988, *J. Amer. chem. Soc.*, **110**, 7991.
[10] GILLIES, C. W., and KUCZKOWSKI, R. L., 1972, *J. Amer. chem. Soc.*, **94**, 6337.
[11] CREMER, D., 1979, *J. chem. Phys.*, **70**, 1928.

[12] CREMER, D., 1979, *J. Amer. chem. Soc.*, **101**, 7189.; CREMER, D., 1983, *The Chemistry of Functional Groups, Peroxides*, edited by S. Patai (New York: Wiley), p. 1.

[13] CREMER, D., 1981, *J. Amer. chem. Soc.*, **103**, 3619, 3627, 3633; *Angew. Chem. Int. Edn Engl.*, **20**, 888.

[14] FRANCISCO, J. S., and WILLIAMS, I. H., 1985, *Chem. Phys.*, **95**, 71.

[15] GAUSS, J., and CREMER, D., 1987, *Chem. Phys. Lett.*, **133**, 420.

[16] CREMER, D., SCHMIDT, T., GAUSS, J., RADHAKRISHNAN, T. P., 1988, *Angew. Chem. Int. Edn Engl.*, **27**, 427.

[17] GAUSS, J., and CREMER, D., 1989, *Chem. Phys. Lett.*, **163**, 549.

[18] CREMER, D., SCHMIDT, T., SANDER, W., and BISCHOF, P., 1989, *J. org. Chem.*, **54**, 2515.

[19] BACH, R. D., ANDRÉS, J. L., OWENSBY, A. L., SCHLEGEL, H. B., and MCDOUALL, J. J. W., 1992, *J. Amer. chem. Soc.*, **114**, 7207.

[20] CREMER, D., GAUSS, J., KRAKA, E., STANTON, J. F., and BARTLETT, R. J., 1993, *Chem. Phys. Lett.*, **209**, 547.

[21] CREMER, D., KRAKA, E., MCKEE, M. L., and RADHAKRISHNAN, T. P., 1991, *Chem. Phys.*, *Lett.*, **187**, 491.

[22] LOVAS, F. J., and SUENRAM, R. D., 1977, *Chem. Phys. Lett.*, **51**, 453; SUENRAM, R. D., and LOVAS, F. J., 1978, *J. Amer. chem. Soc.*, **100**, 5117.

[23] MURRAY, R. W., 1989, *Chem. Rev.*, **89**, 1187, and references therein.

[24] ADAM, W., CURI, R., NUNEZ, M. E. G., and MELLO, R. 1991, *J. Amer. chem. Soc.*, **113**, 7654.

[25] SODEAU, J. R., and WHYTE, L. J., 1991, *J. chem. Soc. Faraday Trans.*, **87**, 3725.

[26] HUZINAGA, S., 1965, *J. chem. Phys.*, **42**, 1293.

[27] DUNNING JR., T. H., 1970, *J. chem. Phys.*, **53**, 2823.

[28] DUNNING JR., T. H., 1971, *J. chem. Phys.*, **55**, 716.

[29] DUNNING JR., T. H., 1989, *J. chem. Phys.*, **90**, 1007.

[30] YAMAGUCHI, Y., OSAMURA, Y., GODDARD, J. D., and SCHAEFER III, H. F., 1994, *A New Dimension to Quantum Chemistry: Analytical Derivative Methods in Ab Initio Molecular Electronic Structure Theory* (New York: Oxford University Press).

[31] BROOKS, B. R., LAIDIG, W. D., SAXE, P., GODDARD, J. D., YAMAGUCHI, Y., and SCHAEFER III, H. F., 1980, *J. chem. Phys.*, **72**, 4652.

[32] LANGHOFF, S. R., and DAVIDSON, E. R., 1974, *Int. J. Quantum Chem.*, **8**, 61.

[33] RAGHAVACHARI, K., TRUCKS, G. W., POPLE, J. A., and HEAD-GORDON, M., 1989, *Chem. Phys. Lett.*, **157**, 479.

[34] SCHEINER, A. C., SCUSERIA, G. E., RICE, J. E., LEE, T. J., and SCHAEFER III, H. F., 1987, *J. chem. Phys.*, **87**, 5361.

[35] SAXE, P., YAMAGUCHI, Y., and SCHAEFER III, H. F., 1982, *J. chem. Phys.*, **77**, 5647.

[36] JANSSEN, C. L., SEIDL, E. T., SCUSERIA, G. E., HAMILTON, T. P., YAMAGUCHI, Y., REMINGTON, R. B., XIE, Y., VACEK, G., SHERRILL, C. D., CRAWFORD, T. D., FERMANN, J. T., ALLEN, W. D., BROOKS, B. R., FITZGERALD, G. B., FOX, D. J., GAW, J. F., HANDY, N. C., LAIDIG, W. D., LEE, T. J., PITZER, R. M., RICE, J. E., SAXE, P., SCHEINER, A. C., and SCHAEFER III, H. F., 1994, PSI 2.08 (Watkinsville, GA: Psitech Inc.).

[37] CREMER, D., KRAKA, E., and SZABO, K. J., 1995, *The Chemistry of the Cyclopropyl Group*, edited by Z. Rappoport, (New York: Wiley).

[38] MURRAY, R. W., and JEYARAMAN, R., 1985, *J. org. Chem.*, **50**, 2847.

[39] CREMER, D., and SCHINDLER, M., 1987, *Chem. Phys. Lett.*, **133**, 293; ADAM, W., CHAN, Y.-Y., CREMER, D., GAUSS, J., SCHEUTZOW, D., and SCHINDLER, M., 1987, *J. org. Chem.*, **52**, 2800.

[40] BUCHER, G. and SANDER, W., 1992, *Chem. Ber.*, **125**, 1851, and references therein.

[41] SANDER, W., private communication.

[42] RUSSO, A., and DESMARTEAU, D. D., 1993, *Angew. Chem. Int. Edn Engl.*, **32**, 905.

[43] KRAKA, E., and CREMER, D., unpublished; see also RAHMAN, M., MCKEE, M. L., SHEVLIN, P. B., and SZTYRBISKA, R., 1988, *J. Amer. chem. Soc.*, **110**, 4002.