MR-CISD AND MR-AQCC CALCULATION OF EXCITED STATES OF MALONALDEHYDE: GEOMETRY OPTIMIZATIONS USING ANALYTICAL ENERGY GRADIENT METHODS AND A SYSTEMATIC INVESTIGATION OF REFERENCE CONFIGURATION SETS

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Dedicated to Professors Petr Čársky, Ivan Hubač and Miroslav Urban on the occasion of their 60th birthdays.

Extended MR-CISD and MR-AQCC calculations have been performed on the ground state and the first two excited states of malonaldehyde. Full geometry optimizations have been carried for C_s and C_{2v} structures both at MR-CISD and MR-AQCC levels. Vertical and minimum-to-minimum excitation energies and oscillator strengths have been computed. Systematic studies have been undertaken concerning several types of reference spaces. Agreement with the experimental 0-0 transition energy to the S_1 state (expt. 3.50 eV, calc. 3.56 eV) and for the vertical excitation to S_2 (expt. band maximum 4.71 eV, best estimate 4.86 eV) is very good. In agreement with the CASSCF/CASPT2 results by Sobolewski and Domcke (*J. Phys. Chem. A* **1999**, *103*, 4494), we find that the hydrogen bond in malonaldehyde is weakened by excitation to the S_1 state. The barrier for proton transfer in the S_1 state is increased in comparison with the ground state.

Keywords: Excited states; Multireference configuration interaction; Proton transfer; Hydrogen bond; Malonaldehyde; *Ab initio* calculations.

Malonaldehyde (MA) is an important prototype system for studies of intramolecular proton transfer (PT) processes. In the ground state, the PT takes place *via* a tunneling mechanism between two equivalent C_s structures at a relatively low barrier height of about 6.6 kcal/mol [1]. The top of the barrier is represented by a C_{2v} structure in which the migrating hydrogen atom is located in the middle between the two oxygen atoms. Several

ab initio investigations (see refs[2–4]) have been performed in order to compute this barrier. Barrier heights in the range between 4–6 kcal/mol were obtained. Calculated energy surfaces have been used in dynamics calculations to evaluate the tunnel splitting[3,5] and IR spectra[6]. Analysis of these investigations shows that the PT process in the electronic ground state is a complex, multidimensional process.

The situation is even more complicated for PT in excited states. From the splitting of the band origin in the $n{\to}\pi^*$ (S_1) transition, the tunnel splitting in the excited state was derived. From this splitting the barrier height for PT in the S_1 state in comparison with that in the ground state was deduced. Different values of 7 cm^{-1} by Seliskar and Hoffman[7] and of 19 cm^{-1} by Arias *et al.*[8] for the splitting of the band origin have been reported. In particular the last value would have lead to a significant increase in the barrier height for PT in the S_1 state. *Ab initio* calculations using the method of configuration interaction with singles (CIS) by Luth and Scheiner[9] showed a significant increase in the barrier in the S_1 state and a decrease in the S_2 ($\pi{\to}\pi^*$) state. However, both barriers disappeared in subsequent calculations by the same authors based on Møller–Plesset corrections to second order (MP2). This disappearance of the barrier in the CIS-MP2 calculations motivated Arias *et al.*[8] to a reinterpretation of their results leading to an increase in the tunnel splitting and a decrease in the PT barrier in S_1 relative to S_0.

Extended complete active space self-consistent field (CASSCF) and complete active space perturbation theory to second-order (CASPT2) investigations have been performed by Sobolewski and Domcke[10] on the PT and proton detachment (PD) processes in the S_1 and S_2 states. Sobolewski and Domcke showed that the appropriate choice of the CAS is crucial for reliable results. Dynamic electron correlation computed using the CASPT2 approach was found to be important. A significant increase in the barrier height for PT from 3.1 kcal/mol for the ground state to 8.6 kcal/mol for the S_1 state was observed at the CASPT2 level. For the S_2 state, no barrier to PT existed and the most stable, planar structure was of C_{2v} symmetry.

In addition to PT, Sobolewski and Domcke[10] investigated the PD process as well. It was shown by these authors that additional states involving $n{\to}\sigma^*$ and $\pi{\to}\sigma^*$ excitations were of crucial importance. They form conical intersections with the $\pi{\to}\pi^*$ and $n{\to}\pi^*$ states and with the ground state. It was suggested by Sobolewski and Domcke that this system of conical intersections could be regarded as a prototype for many photochemical and photophysical processes in nucleic bases and aromatic amino acids[11,12].

The quantum chemical calculation of the potential energy surfaces for the PD process is significantly more involved than that for the PT because

of the conical intersections encountered in this case. The single-state CASSCF and CASPT2 approach used by Sobolewski and Domcke[10] could only be applied in limited, discontinuous sections of the PD reaction coordinate as long as the wave function was dominated by one state only. State-averaged multiconfiguration SCF (SA-MCSCF) in combination with multireference configuration interaction with singles and doubles (MR-CISD) has the appropriate generality to resolve the above-mentioned problems. State averaging at the MCSCF level provides for a balanced set of molecular orbitals (MOs) and the MR-CISD approach based on such MOs is well suited for a simultaneous calculation of a multitude of states. Size-extensivity corrections are important and can be computed by means of the generalized Davidson method[13,14] or in a more general and consistent way by the multireference averaged quadratic coupled cluster (MR-AQCC) method[15,16], which is closely related to the multireference averaged coupled pair functional (MR-ACPF) approach[17]. The availability of analytical energy gradients with respect to nuclear coordinates is another major advantage of the MR-CISD and MR-AQCC methods (see refs[18,19] and further references therein). Recently, efficient methods and computer programs have been developed for analytical MR-CISD/MR-AQCC gradients within the COLUMBUS project[20–22] under special consideration of excited states and MCSCF state-averaging[23]. Thus, geometries can be optimized now at a considerably higher methodological level in multireference cases as compared to the usual CASSCF geometry optimizations.

MR-CISD/MR-AQCC calculations are computationally much more demanding than comparable CASPT2 computations. Therefore, the selection of appropriate reference spaces, which determine the accuracy and the efficiency of the calculation, is very important. It was the purpose of this work to investigate systematically different choices of active orbital spaces and reference configuration sets and to assess the accuracy of results. Basis set effects were studied as well. Full MR-CISD and MR-AQCC geometry optimizations were performed for all planar, stationary points involved in the PT process in the S_0, S_1 and S_2 states as determined by Sobolewski and Domcke[10]. Vertical and adiabatic excitation energies were computed and compared with experimental data as far as available. Based on the experience gained in these calculations, investigations on potential energy curves for the PD process are currently being performed in our group.

COMPUTATIONAL

MR-CISD [24], MR-CISD+Q [13,14] (generalized Davidson method) and MR-AQCC [15,16] calculations have been performed on the S_0, S_1 and S_2 states of malonaldehyde. The first computational step consists of a state-averaged MCSCF calculation, where the same weights are given to all three states. The active space contains ten electrons and eight orbitals (CAS(10,8)), namely, $9a_1(\sigma)$, $7b_2(n)$, $1b_1(\pi)$, $1a_2(\pi)$, $2b_1(\pi)$, $3b_1(\pi^*)$, $2a_2(\pi^*)$ and $10a_1(\sigma^*)$. These MCSCF orbitals are used in subsequent MR-CISD and MR-AQCC calculations. This CAS(10,8) is the same as the "medium" CAS used by Sobolewski and Domcke[10].

Based on these CASSCF MOs several reference configuration sets for the MR-CISD and MR-AQCC calculations were investigated. A *small* reference space was constructed as a CAS(6,5) with the $7b_2(n)$, $2b_1(\pi)$, $1a_2(\pi)$, $3b_1(\pi^*)$ and $2a_2(\pi^*)$ orbitals. The 4-9 a_1, $1b_1(\pi)$ and 3-6 b_2 orbitals were kept doubly occupied in the reference configurations, but included in the CI treatment. The 1-3 a_1 and 1-2 b_2 core orbitals (C and O 1s orbitals) were frozen in all post-MCSCF calculations. The final expansion space for the MR-CISD and MR-AQCC calculations was constructed from the reference configuration state functions (CSFs) and all single and double excitations thereof into all virtual orbitals. In the procedure for the construction of the single and double substitutions, three cases were distinguished. In the standard approach, only reference configurations having the same symmetry as the state to be computed were selected and the interacting space restriction was applied[25]. This mode gives the smallest CSF expansion size from the three alternatives and is not separately indicated in the designation of the reference space. The second choice aimed at a balanced description of reference configurations for states of different symmetry. This situation occurred when adiabatic energy differences were calculated between the ground state in C_s symmetry and a C_{2v} structure. In order to obtain a compatible set of reference configurations in terms of symmetry, for both states the symmetry elements of the state with lower symmetry (in our case this was the symmetry plane σ_h ($\equiv \sigma_{yz}$) of C_s) were considered only for the selection of reference configurations. Thus, for the $^1B_1$ state, the reference symmetries B_1 and A_2 correlating with A'' were selected and for the $^1B_2$ state the reference symmetries A_1 and B_2 (correlating with A') were chosen. The calculations were carried out using the actual symmetry of each molecule. Even though CSFs of the "wrong" symmetry were included, certain single and double excitations thereof have the correct symmetry of the state again. This procedure is identical to computing both states at the same lower symmetry. The advan-

tage of the current procedure is that the computational benefits of the higher symmetry are preserved. The interaction space restriction was not used. Test calculations showed that the increase in the number of reference symmetries was significantly more important for the calculation of excitation energies than the removal of the interacting space restriction. This second mode for the construction of the reference space is indicated by "+", as, *e.g.* in *small+*. In the third alternative, all possible reference symmetries were allowed. This is indicated by "*f*", such as in *small-f*.

The *medium* reference space contains additional $9a_1(\sigma)$, $10a_1(\sigma^*)$ and $1b_1(\pi)$ active orbitals leading to a CAS(10,8) and is identical to the CAS space of the CASSCF calculation. The same procedures and nomenclature as before was applied as described for the *small* reference space. The configuration space in the *medium-f* reference case was already quite large in C_s symmetry (more than 400 million). Therefore, additional occupation restrictions were imposed on those orbitals, which had been added to the *small* reference space. Starting from the list of CAS orbitals ordered as $9a_1(\sigma)$, $1b_1(\pi)$, $7b_2(n)$, $1a_2(\pi)$, $2b_1(\pi)$, $3b_1(\pi^*)$, $2a_2(\pi^*)$ and $10a_1(\sigma^*)$, the first two ($9a_1(\sigma)$, $1b_1(\pi)$) were transferred to a restricted active space (RAS) and the last one to an auxiliary (AUX) space. Starting from the list of reference CSFs for the full *medium* CAS, only single excitations were allowed from the RAS into the remaining active orbitals (CAS+AUX) and single occupancies in AUX were included only in the process for the construction of reference configurations for the *medium(s)* reference space. From this list of references, all single and double excitations into all virtual orbitals were generated again. For *medium(s)* the subdivisions *medium(s)+* and *medium(s)-f* were constructed as explained before for the other reference spaces.

Several MR-AQCC excited-state calculations showed intruder-state problems, *i.e.* few (maximum five), additional CSFs not contained in the reference space obtained an unreasonably large weight. In order to resolve this problem, these individual CSFs were included in the reference space as well.

All geometries have been fully optimized at MR-CISD and MR-AQCC levels of theory, employing the *small* reference space for that purpose. Full geometry optimizations were performed within given molecular symmetries in natural internal coordinates[26] using the GDIIS method[27]. Single-point energy calculations have been performed at the MR-CISD geometries, using the reference spaces described above. The COLUMBUS program system[20–22] was used for all calculations. Geometry optimizations were performed by means of the analytical MR-CISD and MR-AQCC gradient methods[18,19,23]. The CSF expansion spaces for the MR-CISD and MR-AQCC calculations

range from about 1.4 million (C_{2v} symmetry with *small*/6-31G**) to 270 million (C_s symmetry with *medium*+/6-31G**). The larger calculations were carried on the Linux PC cluster Schrödinger I of the University of Vienna using the newly-developed parallel CI program[28] based on the concepts of a previous parallel version developed by Dachsel *et al.*[29] Each node of the cluster is equipped with an AMD Athlon XP 1700+ processor, of 1 GB central memory and 40 GB disk space. Up to 32 nodes were used in individual calculations.

The atomic orbital (AO) integrals and AO gradient integrals have been computed with program modules taken from DALTON [30]. The 6-31G** valence double-ζ basis set[31] with polarization functions on all atoms has been used for all geometry optimizations. Three additional, extended basis sets have been selected for single-point calculations: the 6-311G** basis set[32], the 6-31+G** basis[33] and a composed basis, denoted as 6-31G(2d,1p/2p), in which two sets of polarization functions (2d,2p) with exponents taken from the 6-31G(2d,2p) basis[34] were placed on the heavy atoms and the hydrogen atom in the hydrogen bridge, and one polarization function (1p) with the exponent taken from the 6-31G** basis was put onto the remaining hydrogen atoms. The purpose of the first two, additional basis sets is to explore the effect of expanding the s and p part of the basis and that of the second one to determine the effect of additional polarization functions.

RESULTS AND DISCUSSION

Calculated geometry parameters for structures of C_s symmetry and those for C_{2v} symmetry are collected in Tables I and II, respectively. For comparison, results from previous CASSCF optimizations are also presented. MP2 and experimental results are given for the ground state. The atom-numbering scheme is shown in Fig. 1. The C_s structures given in Table I are the minima on the energy surfaces of the S_0 and S_1 states. The C_{2v} structures for the S_0 and S_1 states are the saddle points for PT. The C_{2v} structure for the S_2 state corresponds to a minimum subject to planarity restriction of the malonaldehyde molecule. For more details concerning the general characterization of the molecular structures, see ref.[10]

The effect of size-extensivity contributions on geometries can be seen from a comparison of MR-CISD and MR-AQCC results. Bond distances are usually stretched by about 0.01 to 0.02 Å in MR-AQCC calculations as compared to MR-CISD. An exception is the intramolecular hydrogen bond distance $O_4\cdots H_7$ in the structures of C_s symmetry, for which much larger changes around 0.07 to 0.1 Å are observed. This bond distance is very sensi-

TABLE I
MR-CISD and MR-AQCC geometrical parameters for C_s structures calculated with the small reference space and the 6-31G** basis set in comparison to previously computed and experimental results (distances in Å and angles in °)[a]

Geometry	S_0 (1^{1}A')					S_1 (1^{1}A'')		
	CI	AQCC	MP2 [2]	CASSCF [10]	exp.	CI	AQCC	CASSCF [10]
O5-H7	0.965	0.985	0.994	0.951	(0.969)[b]	0.954	0.964	0.945
C3-O5	1.323	1.338	1.328	1.327	1.320	1.359	1.369	1.378
C1-C3	1.356	1.370	1.362	1.349	1.348	1.389	1.393	1.391
C1-C2	1.452	1.444	1.439	1.465	1.454	1.387	1.398	1.379
C2-O4	1.231	1.247	1.248	1.213	1.234	1.359	1.355	1.361
O4-H7	1.861	1.754	1.694	1.978	1.68	2.135	2.064	2.182
C3-H9	1.077	1.083	1.083	1.075	1.089	1.072	1.079	1.070
C1-H6	1.074	1.080	1.077	1.074	1.091	1.076	1.081	1.075
C2-H8	1.092	1.100	1.098	1.094	1.094	1.076	1.086	1.072
C2-C1-C3	121.1	120.0	119.5	123	119.4	128.0	126.5	129
C1-C2-O4	123.5	123.9	123.5	124	123.0	122.2	122.5	123
C1-C3-O5	126.0	124.6	124.5	126	124.5	126.4	125.9	127
C3-O5-H7	108.2	106.2	105.4	110	106.3	111.5	110.4	112
C1-C3-H9	121.5	122.6	122.5	121	122.3	121.5	121.9	121
C1-C2-H8	117.2	117.3	117.6	116	117.6	124.6	123.7	125

[a] Total energies (a.u.): S_0, CI: -266.42501; S_1, CI: -266.18321, AQCC: -266.29014. [b] Assumed value.

tive to the values of the skeletal valence angles of malonaldehyde and relatively small changes in these angles can effect large changes in the $O_4 \cdots H_7$ bond distance. For the ground state, agreement with the MP2 results[2] and experimental microwave structure[35] is good. Both MR-AQCC and MP2 methods show a slightly smaller value for the O_5–H_7 bond distance than the one assumed in the analysis of the microwave spectrum (see Table I). Agreement between the MR-AQCC and CASSCF values of Sobolewski and

TABLE II
MR-CISD and MR-AQCC geometrical parameters for C_{2v} structures calculated with the *small* reference space and the 6-31G** basis set in comparison to previously computed (distances in Å and angles in °)[a]

Geometry	S_0 (1^1A_1)			S_1 (1^1B_1)		S_2 (1^1B_2)		
	CI	AQCC	MP2 [2]	CI	AQCC	CI	AQCC	CASSCF [10]
05–H7	1.190	1.202	1.203	1.150	1.174	1.198	1.221	1.255
C3–O5	1.271	1.288	1.285	1.353	1.361	1.286	1.312	1.301
C1–C3	1.395	1.403	1.396	1.383	1.393	1.465	1.458	1.441
C3–H9	1.084	1.090	1.089	1.074	1.082	1.077	1.084	1.074
C1–H6	1.071	1.078	1.075	1.073	1.078	1.073	1.081	1.073
C2–C1–C3	115.5	115.7	–	116.5	116.6	117.6	118.8	120
C1–C2–O4	121.7	121.7	121.9	119.2	119.7	118.0	118.3	119
C3–O5–H7	102.1	101.6	101.2	106.7	106.3	103.1	102.3	101
C1–C3–H9	121.4	121.5	–	126.8	126.2	122.4	122.8	123

[a] Total energies (a.u.): S_0, CI: –266.29401, AQCC: –266.41916; S_1, CI: –266.13143, AQCC: –266.26412; S_2, CI: –266.10779, AQCC: –266.24730.
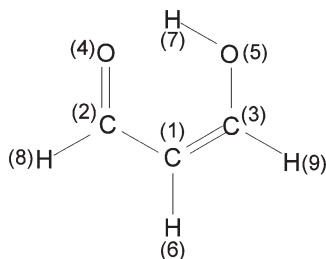

FIG. 1
Atom-numbering scheme for the malonaldehyde molecule

Domcke[10] is also quite satisfactory (within a few hundredths of Å) for all electronic states except for the already mentioned hydrogen bond distance $O_4\cdots H_7$ in the C_s structures given in Table I. CASSCF gives values, which are too large between 0.22 (S_0) and 0.12 Å (S_1). Nevertheless, we confirm the observation of Sobolewski and Domcke[10] that the hydrogen bond is weakened by excitation to the S_1 state because of the stretching of the hydrogen bond. For the symmetric hydrogen bond in the C_{2v} structure of S_2, the deviation between MR-AQCC and CASSCF is significantly reduced to 0.03 Å.

Vertical excitation energies are given in Table III. By inspection of this table one can clearly note the systematic decrease in the excitation energy with the number of reference configurations. This reduction is observed within a series for a given type of active orbitals (*e.g. small → small+ → small-f*) and for increasing active orbital sets. In the latter case, compare for

TABLE III
Vertical excitation energies (in eV) calculated at MR-CISD, MR-CISD+Q and MR-AQCC levels using several reference spaces and basis sets[a,b]

Reference space	S_1 ($1^1A''$)			S_2 ($2^1A'$)		
	CI[c]	CI+Q	AQCC	CI[c]	CI+Q	AQCC
small [b]	4.27 (6.9×10^{-5})	4.25	4.15	6.00 (0.31)	5.58	5.38
small+ [b]	4.25	4.20	–	5.98	5.52	–
small-f [b]	4.22	4.14	–	5.95	5.47	–
medium(s) [b]	4.25 (8.7×10^{-5})	4.24	4.17	5.65 (0.25)	5.37	5.16
medium(s)+ [b]	4.23	4.18	4.13	5.64	5.34	5.12
medium(s)-f [b]	4.19	4.07	4.06	5.63	5.32	–
medium [b]	4.26	4.24	4.19	5.60	5.38	5.15
medium(s)+6-311G**	4.15	4.09	–	5.60	5.30	–
medium(s)+6-31+G**	4.11	4.10	–	5.59	5.23	–
medium(s)+6-31G(2d,1p/2p)	4.19	4.05	–	5.61	5.23	–
Best estimate this work[d]		3.76				4.86
CASPT2 [10]		3.83				4.51

[a] The MR-CISD geometry given in Table I was used. [b] 6-31G** basis calculations unless indicated differently. [c] Oscillator strength given in parentheses. [d] See the text.

consistency the numbers for each type of reference space separately, *i.e.* either the series *small* → *medium(s)* → *medium* or *small+* → *medium(s)+* or *small-f* → *medium(s)-f*. In the case of S_1, changes of excitation energies within a given active orbital space amount up to 0.17 eV for the 6-31G** basis set. Differences between corresponding values for different active orbital sets are mostly smaller. Size-extensivity effects (*cf.* MR-CISD and MR-AQCC values) amount to around 0.1 eV. The MR-CISD+Q values lie in between. Basis set effects are non-negligible (compare the different *medium(s)+* results in Table III). The excitation energy for S_1 is reduced by 0.09 eV using the 6-311G** basis, by 0.08 eV using the 6-31G+** basis and by 0.13 eV for the 6-31G(2d,1p/2p) basis as compared with the standard 6-31G** basis set. These results show that diffuse functions included in the 6-31G+** basis set have a non-negligible contribution. Since the three basis set extensions performed here refer to different aspects of improvement, we take as total basis set effect the accumulated value of 0.30 eV. This is probably overshooting the current basis set effects, but it should take into account in a very approximate way the influence of remaining basis set inadequacies. Subtracting this value from the MR-AQCC/*medium(s)-f* value of 4.06 eV gives an estimate of 3.76 eV for the vertical excitation energy to S_1.

In the case of S_2, effects on excitation energies due to increase in the reference space are larger than was observed for the S_1 state. Going from the *small* reference space to *medium(s)* results in changes of about 0.2 eV (MR-CI+Q and MR-AQCC results). However, moving further from *medium(s)* to the full *medium* space leads only to negligible additional changes. This demonstrates that the *medium(s)* space is already quite flexible and constitutes a good approximation to the full *medium* space. The size-extensivity effect on the excitation energy of the S_2 state is significantly more pronounced than for the S_1 excitation. The effect of the Davidson correction *via* MR-CISD+Q amounts to about 0.3 eV (*medium(s)* cases). The MR-AQCC method gives an additional reduction of about 0.2 eV. Thus, it can be seen that especially in this case of excitation to S_2, the MR-CISD method itself leads to very unsatisfactory results. The maximum deviation (MR-CISD/*small vs* MR-AQCC/*medium(s)-f*) is 0.9 eV. Switching from the *small* to *medium(s)* reference space improves the situation, but the discrepancies are still about 0.5 eV. Basis set effects (accumulated value 0.26 eV, see MR-CISD+Q/*medium(s)+* results) are comparable with the S_1 case. As in the case of S_1 state, we take this value as a first estimate of the total basis set effect. Thus, we obtain from the MR-AQCC/*medium(s)+* value of 5.12 eV for the vertical excitation energy of S_2 a corrected energy of 4.86 eV. This value

compares well with the experimentally found maximum at 4.71 eV [36] of a vibrationally unresolved band in the vapor phase UV spectrum.

Comparing our MR-AQCC/6-31G** results with the CASPT2 values reported by Sobolewski and Domcke[10] using the same basis set (see Table III), one finds that our vertical excitation energy for the S_1 state of 4.06 eV (MR-AQCC/*medium*(*s*)-*f*) is higher by 0.23 eV than the CASPT2 result. No experimental value exists in this case. For the vertical S_2 excitation the discrepancy of 0.61 eV (compare the MR-AQCC/*medium*(*s*)+ 6-31G** value of 5.12 eV with the CASPT2 result of 4.51 eV) is much larger. Assuming similar basis set effects for the CASPT2 method as was found in our calculations (approx. –0.25 eV) would have the effect that the CASPT2 value of 4.51 eV would be reduced and thus moved away from the experimental value. This finding is in agreement with the observation of Sobolewski and Domcke[10] that CASPT2 overstabilizes the S_2 state. In Table III oscillator strengths are given as well. They are very small for the S_1 state ($\approx 10^{-4}$) and ≈ 0.25 for the S_2 state. These values agree well with the results of Sobolewski and Domcke[10] and with the experimental value ≈ 0.3 for S_2 [36].

In Table IV minimum-to-minimum excitation energies with respect to the S_0 ground state are collected. The energy differences in the columns for S_0 represent the energy barrier for PT on the ground-state surface. The MR-AQCC value 0.152 eV agrees quite well with the CASPT2 value of 0.136 eV reported by Sobolewski and Domcke[10]. Other, computationally simpler methods could be used if only the ground state surface were to be calculated. Since we were interested in the excited states, we did not pursue the question of the ground-state barrier further.

The analysis of the dependence of minimum-to-minimum excitation energies on reference spaces and basis sets can be carried out similarly to the one performed for vertical excitations. We refer the reader to Table IV for details. From this table one can see that the excitation energy for the C_s ($1^1A''$) minimum structure is rather insensitive to the size of the reference space. However, it is noteworthy that extension of the reference space from *small* to *medium*(*s*) increases the excitation energy for the C_s ($1^1A''$) state by about 0.1 eV and less, in contrast to all other excited states and geometries investigated in this work, where the increase in the reference space led to a decrease in the excitation energy. There is almost no difference between *medium*(*s*) and *medium* results. Size-extensivity effects also increase the excitation energies slightly, again in opposition to all other cases. In contrast to vertical excitations, basis set effects are practically negligible here. This is also true for the remaining structures given in Table IV. Our most reliable

Table IV
Minimum-to-minimum excitation energies[a] (in eV) calculated at MR-CISD, MR-CISD+Q and MR-AQCC levels using several reference spaces and basis sets

Reference space	S_0, C_{2v} (1^1A_1)			S_1, C_s ($1^1A''$)			S_1, C_{2v} (1^1B_1)			S_2, C_{2v} (1^1B_2)		
	CI	CI+Q	AQCC	CI	CI+Q	AQCC	CI	CI+Q	AQCC	CI	CI+Q	AQCC
small[b]	0.489	0.364	0.152	3.50	3.62	3.65	4.91	4.62	4.37	5.56	5.06	4.85
small+[b]	–	–	–	3.50	3.62	–	4.77	4.35	–	5.38	4.71	–
small-f[b]	–	–	–	3.50	3.61	–	4.70	4.18	–	5.31	4.58	–
medium(s)[b]	0.322	0.292	–	3.64	3.71	3.71	4.45	4.40	4.26	4.86	4.76	4.68
medium(s)+[b]	–	–	–	3.63	3.69	3.70	4.36	4.22	4.06	4.75	4.57	4.38
medium(s)-f[b]	–	–	–	3.62	3.66	3.68	4.31	4.10	4.07	4.74	4.55	4.34
medium[b]	–	–	–	3.64	3.71	3.73	4.49	4.39	4.28	4.83	4.73	4.64
medium+[b]	–	–	–	3.63	3.68	3.70[e]	4.40	4.22	4.10[e]	4.74	4.57	4.40[e]
medium(s)+[c]	–	–	–	3.64	3.69	–	4.34	4.20	–	4.75	4.54	–
medium(s)+[d]	–	–	–	3.66	3.72	–	4.36	4.23	–	4.74	4.55	–
CASPT2 [10]			0.136			3.38			3.89			3.95

[a] Relative to the ground state using the MR-CISD structure (C_s), see Table I. [b] 6-31G** basis. [c] 6-311G** basis. [d] 6-31G(2d,1p/2p) basis. [e] Best value.

value for the S_1 ($1^1A''$) state is 3.70 eV (MR-AQCC/*medium*+). Correcting for zero-point energies by 0.14 eV using the harmonic CASSCF frequencies of Sobolewski and Domcke[10] results in a 0-0 excitation energy of 3.56 eV, very close to the experimental value of 3.50 eV [7]. The CASPT2 value of 3.38 eV reported by Sobolewski and Domcke[10] for the minimum-to-minimum energy difference is by 0.12 eV too low and would be further decreased by the zero-point-energy correction. The barrier for the PT process computed as the difference between the energies for the planar S_1 (C_{2v}) and S_1 (C_s) structures is 0.40 eV at the *medium*+ level. This number has to be compared with the value of 0.51 eV computed by Sobolewski and Domcke[10]. It should be noted here that the true saddle point in the CASSCF calculations has a nonplanar structure of C_2 symmetry[10] with a CASPT2 barrier height of 0.38 eV.

For the structures of C_{2v} symmetry on the S_1 and S_2 potential energy surfaces, a considerably larger dependence of excitation energies on extension of the reference space and on size-extensivity corrections is observed as compared with the S_1 structure of C_s symmetry (see Table IV). This effect significantly decreases in the series *small* → *medium*(*s*) → *medium*, with the greatest variations occurring from *small* to *medium*(*s*) showing that the latter is a very good compromise in terms of accuracy and computational efficiency. Comparison of excitation energies within a given active orbital space (see, *e.g.*, MR-AQCC values in the *medium*(*s*) series of the S_2 state in Table IV) demonstrates the importance of the choice of reference symmetries: the energy difference between *medium*(*s*) and *medium*(*s*)+ is 0.30 eV, but the change between *medium*(*s*)+ and the complete *medium*(*s*)-*f* reference space is only 0.04 eV. The situation is very similar in other, comparable cases. The reason for this behavior lies in the unbalanced influence of symmetry in the case when only one reference symmetry is used (see the discussion in the section Computational). This has different effects when geometries of different symmetry (C_s symmetry for the ground state and C_{2v} symmetry for the excited state) are considered. Inclusion of equivalent numbers of reference symmetries leads to a drastically improved balance in the calculation. When structures of the same symmetry are compared (vertical excitations or minimum-to-minimum excitation to the S_1 (C_s) state), this kind of imbalance is absent. Comparison of our MR-AQCC energies of the C_{2v} structures for S_1 and S_2 with the respective CASPT2 values of Sobolewski and Domcke[10] shows that also in this case the latter values are smaller (probably too low) by about 0.2 eV (S_1) and 0.45 eV (S_2), respectively.

CONCLUSIONS

For the first time excited-state geometries of malonaldehyde have been fully optimized at the post-CASSCF level using the MR-CISD and MR-AQCC methods. Usual, systematic differences between MR-CISD and MR-AQCC geometries are found. Agreement between our optimized geometries and the CASSCF results from ref.[10] is quite good. Typical differences in bond distances are in the range of a few hundredths of Å. The major exception is the hydrogen bond distance in the C_s structures of the S_0 and S_1 states where differences of 0.1 to 0.2 Å are observed. In agreement with the CASSCF geometries of Sobolewski and Domcke[10], we find that the hydrogen bond distance is significantly stretched (by about 0.3 Å) upon excitation to the S_1 state and thus significantly weakened.

The effect of extension of the reference space was studied systematically. In addition to the *small* CAS, containing the $7b_2(n)$, $1a_2(\pi)$, $2b_1(\pi)$, $3b_1(\pi^*)$, $2a_2(\pi^*)$ orbitals, a *medium* CAS was constructed including additionally the $9a_1(\sigma)$, $1b_1(\pi)$ and $10a_1(\sigma^*)$ orbitals. It was shown that the *medium* CAS could be significantly reduced to *medium(s)* without any practical loss in accuracy by imposing orbital occupation restrictions, but with substantially reduced computational cost. This procedure is of general significance and increases the range of applicability of MR-CISD and MR-AQCC calculations considerably. It was shown that a balanced construction of reference configurations required special care in the choice of reference symmetries. When energy differences between two structures of different symmetry were computed, extended sets of reference symmetries had to be used. This point is also of general relevance beyond the current application to malonaldehyde.

Comparison of results obtained with different reference spaces shows that the S_2 state is more difficult to compute than the S_1 state. It has also been shown that size-extensivity corrections are extremely important for excitation energies. The MR-CISD method, even though used with relatively large reference spaces, does not give satisfactory results. For vertical excitations, basis set effects are also significant.

In comparison with spectroscopic data, very good agreement has been found for the 0-0 excitation to the S_1 ($1^1A''$) state. Our best result gives, after inclusion of zero-point energy corrections, an excitation energy of 3.56 eV. The experimental value is 3.50 eV. The uncorrected value of 3.38 eV obtained by Sobolewski and Domcke[10] for the minimum-to-minimum excitations is already somewhat too low. For the vertical excitation to the S_2 state our best estimated value of 4.86 eV is also in good agree-

ment with the experimentally observed band maximum at 4.71 eV. The CASPT2 value of 4.51 eV is too low and would probably be further reduced by extension of the basis set. Thus, we observe – in agreement with the statements of Sobolewski and Domcke[10] – a substantial overstabilization of the S_2 state by the CASPT2 method.

The PT barrier in the S_1 state is 0.40 eV under restriction to planar geometries. This value compares quite well with the 0.51 eV of Sobolewski and Domcke[10]. Thus, the barrier to PT transfer is increased in S_1 as compared with the ground state (about 0.15 eV, this work), even though a decrease of the barrier by ≈0.1 eV has to be expected by out-of-plane deformations[10].

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