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Structure of ketene – Revisited r_e (equilibrium) and r_m (mass-dependent) structures

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ABSTRACT

The structure of ketene has been revisited on the basis of five new investigated isotopologues which, added to the existing six, rise their number to eleven. This gives an useful basis for new discussions about the structure. The quadratic, cubic and semi-diagonal quartic force field of ketene has been calculated at the MP2 level of theory employing a basis set of triple-ζ quality. A semi-experimental equilibrium structure has been derived from experimental ground state rotational constants and rovibrational interaction parameters calculated from the *ab initio* force field. This structure is in excellent agreement with the *ab initio* structure calculated at the CCSD(T) level of theory using a basis set of quintuple-ζ quality and a core correlation correction. The empirical structures including the mass-dependent r_m structures have also been determined and their accuracy is discussed. The $r_m^{(1rL)}$ method is the most stable under several testing conditions. However, the results are still not fully satisfactory. This is mainly due to the small coordinate of the keto-carbon.

1. Introduction

Ketene, $H_2C{=}C{=}O$, is a model molecule to test molecular structure determination methods, force field calculations, studies of vibration–rotation interactions, as well as a model for the elucidation of unimolecular reaction rate theories [1]. The microwave studies of the ketene molecule began 59 years ago in 1950 [2]. In the following years, the ground state rotational constants of five isotopologues were determined and employed for structure determinations [3–5]. In 1987, Duncan and Munro [6] obtained an accurate harmonic force field, they calculated an average (r_z) structure and extrapolated it to get an estimate of the equilibrium (r_e) structure. In 1990, after the measurement of a new ketene isotopologue, $H_2C^{13}CO$, in the microwave and millimeter wave range by Brown et al. [7], the rotational constants of six isotopologues were used to calculate empirical r_0 and r_s structures and the r_m^ρ structure which was taken to be an approximate equilibrium structure. In 1995, East et al. [8] published a similar paper where they calculated an *ab initio* anharmonic force field and determined a semi-experimental equilibrium structure using the ground state rotational constants of the six known isotopologues. In 1999 Watson et al. [9] described an improved method for the calculation of mass-dependent structure parameters r_m which should allow an even better approximation to the equilibrium parameters r_e. (Note: in this work the notation r_m is meant to summarize all models with the subscript m and a superscript $(\cdots)$ as discussed in [9]). In [9] the results of one example the $r_m^{(2r)}$ structure calculation of ketene, [9 (Table 10)], were described by the authors as not completely satisfactory when compared to the r_e-parameters of [8]. However, the number of known isotopologues was at that time only six as also in [7] and thus hardly sufficient for the determination of four structural and seven rovibrational parameters with the additional disadvantage that some rotational constants *A* had a large inaccuracy. In 2001 the rotational constants of one further isotopologue, $H_2CC^{17}O$, were measured and a new calculation of the r_0 and r_s structures could be accomplished [10]. In 2003 the spectra of the ketene isotopologues $H_2C^{13}CO$, $H_2{}^{13}CCO$, and $H_2CC^{18}O$ have been revisited and measured up to 350 GHz [11] with the purpose of obtaining for all three isotopologues rotational constants *A* with an accuracy comparable to that of the main isotopologue [12] and of ^{17}O-ketene [10]. Recently, the rotational constants of four further species have been published [13] which increases the number of known ketene isotopologues to 11.

The paper is organized as follows. Section 2 describes the calculation of the *ab initio* structure of ketene. Section 3 is dedicated to the determination of the rotational constants. Section 4 describes the different experimental structures and Section 5, the semi-experimental equilibrium structure.

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2. Ab initio structure

The molecular geometry of ketene has been optimized at the coupled cluster (CC) level theory with single and double excitation [14] augmented by a perturbational estimate of the effects of connected triple excitations [CCSD(T)] [15] using the correlation-consistent polarized valence n-tuple zeta basis sets with $n \in \{\mathrm{D, T, Q}\}$ [16]. It is meanwhile well established that the CCSD(T) technique usually provides reliable structures [17]. As it is not obvious that the structure has converged at the cc-pVQZ level, we have also used a mixed basis set composed of cc-pVQZ on H and cc-pV5Z on the other nuclei. This basis set, denoted cc-pV(Q, 5)Z, leads to a slight loss in accuracy but reduces the computation time. To further reduce computational costs, it was employed only with second-order Møller–Plesset perturbation theory (MP2) [18]. The frozen-core approximation (hereafter denoted as fc), i.e., keeping the 1s orbitals of C and O doubly occupied during correlated-level calculations, was used in these calculations. To estimate the inner-shell correlation effects, the correlation-consistent polarized core-valence n-tuple zeta (cc-pCVnZ) [19,20] basis sets were also employed at the MP2 level. For first row nuclei, it is indeed sufficient to use the MP2 method to estimate this correction [21]. The CCSD(T) calculations were performed with the MOLPRO program package [22] while the MP2 calculations utilized the GAUSSIAN03 (g03) program [23].

At the CCSD(T) level, enlargement of the basis set from cc-pVTZ to cc-pVQZ shows that convergence is almost achieved for the CH internuclear distance and the CCH bond angle but there are non-negligible changes for the other two internuclear distances which are shortened by 0.0025 Å for C=C and 0.0036 Å for C=O, respectively, see Table 1. Upon going from cc-pVQZ to cc-pV5Z at the MP2 level, the C=C internuclear distance decreases very slightly by 0.0006 Å and the C=O internuclear distance by 0.0004 Å indicating that convergence is almost achieved. As O is electronegative, diffuse functions play a significant role when the basis set is small but it is well established that their effect rapidly decreases with the size of the basis set and should thus be negligible at the cc-pV5Z level [24]. To check this point, we have calculated the structure at the MP2 level using a mixed basis set, denoted A'VQZ and composed of cc-pVQZ at H and aug-cc-pVQZ [25] at C and O. Going from VQZ to A'VQZ increases the C=C internuclear distance by 0.0005 Å and the C=O internuclear distance by 0.0006 Å. Correlating all electrons at the MP2/cc-pCVQZ level leads to the expected shortening of the bonds: 0.0014 Å for CH, 0.0032 Å for C=C, and 0.0022 Å for C=O. The best *ab initio* structure (estimate I) may be obtained by adding this core correlation correction to the CCSD(T)/cc-pVQZ structure and by taking into account the effects caused by the basis set enlargement (MP2/cc-pVQZ → MP2/cc-pV(Q, 5)Z). This structure is given in Table 1 as estimate I. As the effect of the diffuse functions was neglected, the C=C and C=O internuclear distances might be slightly too small. Alternatively, taking into account also the effect of diffuse functions at the quadruple zeta level, leads to estimate II. In this case, the C=C and C=O internuclear distances are probably slightly too large.

Table 1
Ab initio structure of ketene (interatomic distances in Å, angles in degrees).

Method[a]	Basis	r(C—H)	r(C=C)	r(C=O)	∠(C=C—H)
CCSD(T)(fc)	VDZ	1.09231	1.3345	1.1763	119.084
CCSD(T)(fc)	VTZ	1.07769	1.3186	1.1670	119.073
CCSD(T)(fc)	VQZ	1.07721	1.3161	1.1632	119.051
CCSD(T)(fc)	V5Z		1.3155	1.1628	
MP2(fc)	VQZ	1.0748	1.3139	1.1643	
MP2(fc)	V(Q, 5)Z[b]		1.3133	1.1640	
MP2(fc)	A'VQZ[b]		1.3144	1.1649	
MP2(fc)	CVQZ	1.0748	1.3136	1.1641	118.952
MP2(ae)	CVQZ	1.0734	1.3104	1.1619	118.995
r_e (estimate I)[b]		1.0758	1.3117	1.1603	119.094
r_e (estimate II)[b]		1.0758	1.3122	1.1609	119.094

[a] fc = frozen-core approximation; ae = all electrons correlated.

[b] See text.

3. Rotational constants

3.1. Spectral details

Table 2 reports the rotational constants and inertial defects of all ketene isotopologues so far investigated and as they appear in [13]. All rotational constants have been obtained taking into account the centrifugal distortion effects up to 8th order through Watson's formalism [26] and are hence rotational constants of the S-reduced Hamiltonian in representation I^r. They are the result of microwave and millimeter wave investigations, however calling on infrared, infrared + microwave, or *ab initio* data for those constants (of minor impact on the frequencies) which are not directly determinable from the microwave data alone. These constants are D_K, H_{KKK}, and H_{JJJ}, see [10,11,13].

The rotational spectra of the H$_2$-isotopologues were predicted from structural calculations based on the rotational constants of the isotopologues reported in [3,7,5,12]. First the $K_a = 3$ doublets at high frequencies were assigned, followed by lines with K_a odd which are, due to spin statistics, three times stronger than lines with K_a even. Through successive fits it was possible to assign all lines up to $K_a = 7$; no relevant deviations from the predicted frequencies were observed. For $K_a \leqslant 7$ the lines could always be found within a few 100 kHz of the predictions, for higher K_a values the well known effect of interactions with the lowest vibrationally excited states through centrifugal distortion [27] became more and more evident. Different fits were performed, changing the maximum value of the K_a quantum number of the lines included from 5 up to 9. The standard error of the fit did not change significantly up to a maximum K_a value of 7, but it increased abruptly when lines with $K_a = 8$ and even more so when lines with $K_a = 9$ were included in the least-squares analysis. In [10 (Fig. 1)], a plot of the different frequencies of the transition $J' = 15 \leftarrow J = 14$ for given values of K_a is reported, comparing the experimental frequencies with the calculated ones (the latter obtained by using the parameters of the fit up to $K_a = 7$).

All presently available rotational constants A, obtained by measuring pure rotational transitions, are within an interval of about 100 MHz with respect to the A value for the parent molecule of [12], where 1700 Fourier-transform combination differences, 300 differences of combination differences, and 250 microwave lines up to $k_a = 9$ were considered. The near agreement of the data is also reflected by similar values of the inertial defects for all H$_2$-isotopologues. The D_K, H_{KKK}, and H_{JJJ} centrifugal distortion constants were fixed at the values of the parent species [12]. The addition of the two octic constants L_{JJKK} and L_{JKKK} to the pool of determinable centrifugal distortion constants led to a better result of the fit compared to that obtained by limiting the constants to sextic order [10,11,13].

For the D$_2$-isotopologues a similar procedure has been used, however the limitation to $K_a \leqslant 7$ was no longer applied because of the changed relation between ground and excited vibrational states. The A constants obtained show a better accuracy and the inertial defects similar values. The centrifugal distortion constants D_K, H_{JJJ}, and H_{KKK} have been fixed at the values stated in the IR report [28]. For the HD-isotopologue the same considerations apply and for the D_K centrifugal distortion constant a value from the IR report [29] is used. For the H_{JJJ} and H_{KKK} a mean value of the two isotopologues H$_2$CCO and D$_2$CCO has been used [13].