



Large scale variational calculations on the vibrational level structure and vibrational mixing in S_0 HDCO up to very high excitation energies

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ABSTRACT

We perform converged high precision variational calculations to determine the exact energies of all vibrational states in S_0 HDCO, extending up to 10000 cm^{-1} of vibrational excitation energy. We also explore the resonances and intermode couplings in this energy range. We compare the calculated level structure to the recently measured frequencies by Ellsworth et al. [K.K. Ellsworth, B.D. Lajiness, J.P. Lajiness and W.F. Polik, *J. Mol. Spectrosc.* 252 (2008) 205] in order to check their assignments and further clarify the vibrational mixing pattern and vibrational resonances in HDCO, that are very different from the other more symmetric formaldehyde species H_2CO and D_2CO . For the calculations we use our specific vibrational method (recently employed for extensive vibrational studies on H_2CO and D_2CO), consisting of a combination of a search/selection algorithm and a Lanczos iteration procedure and based on the Martin, Lee, Taylor potential energy surface for formaldehyde, allowing to extend the calculations up to very high vibrational excitation energies.

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1. Introduction

Formaldehyde H_2CO is a very well known and both photophysically and photochemically interesting molecule [1–3], especially regarding its photochemical activity in urban atmospheres [4], troposphere [5], etc. In addition, H_2CO and its deuterated species HDCO and D_2CO are of major astrophysical importance as well [6,7]. Both the detailed vibrational–rotational structure of formaldehyde in the fundamental domain, that is important for remote identification, as well as the vibrational level structure and mixing at the higher excess vibrational energies (E_v) that is a major factor in photochemical and photophysical conversions, have been studied experimentally extensively and repeatedly using various spectroscopies [1,2,8–12]. From a theoretical point of view, the exact vibrational kinetic energy operator of formaldehyde has been derived by Handy in explicit form already in 1987 [13]. The potential energy surface (PES) of the ground electronic state has also been studied repeatedly by many authors, using both ab initio and empirical approaches [14–18]. All this has made formaldehyde very attractive for the application and testing of various variational, perturbative and algebraic methods designated for calculation of its vibrational level energies [14–16,19–24], that were later transferred to other molecules. A major aim of these calculations has also been the further elaboration and improvement of the

potential energy surface especially at the very high E_v , that are most interesting from a photophysical and photochemical point of view [15,16,18,25,26].

Recently we developed a specific vibrational variational calculation method [27–29], that was based on the exact kinetic energy expression [13] and a PES which is presented in separable (factorized) form. We have already demonstrated [28,29] that our method is able to reproduce with any required precision the vibrational level structure of formaldehyde (corresponding to the employed PES expression) in the lower $E_v < 5000\text{ cm}^{-1}$ domain. The main asset of our method however is, that it allows for converged variational calculations on the vibrational level structure to be carried out at very high excess vibrational energies in formaldehyde-like molecules. In the first applications of this method to formaldehyde H_2CO [28] and formaldehyde D_2CO [29], using the realistic (yielding comparatively good, albeit not exactly spectroscopically accurate calculated vibrational energies) Martin, Lee, Taylor (MLT) quartic PES [17], we were able to perform converged high precision calculations on the vibrational level structure and intramolecular vibrational energy redistribution (IVR) behavior of a large number of vibrational levels, including highly excited CH stretch overtone levels at energies up to $E_v \sim 17000\text{ cm}^{-1}$, where the vibrational level density is quite high. Considerable differences in the IVR behavior and vibrational mixing pattern between the two molecules were found [29].

Formaldehyde HDCO has the same PES as H_2CO and D_2CO (within the Born–Oppenheimer approximation), but a substantially

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different kinetic energy operator, having one H mass and one D mass and reduced molecular symmetry C_s . In contrast to H_2CO and similar to D_2CO , for S_0 HDCO very few experimentally measured frequencies had been available in the lower E_v range, until recently [30–37]. However in 2008 Ellsworth et al. [38] carried out a detailed dispersed fluorescence spectroscopic study on the vibrational level structure of S_0 HDCO that allowed for the observation and assignment of 133 vibrational levels in the range up to $E_v \sim 10000 \text{ cm}^{-1}$.

In our recent work [39] we carried out a preliminary study on the vibrational level structure and vibrational resonances in S_0 HDCO up to 5000 cm^{-1} of excess vibrational energy and compared our calculated energies and assignments with the experimentally measured frequencies and assignments of Ellsworth et al. [38].

Our aim in the present work is to calculate exact energies for all S_0 HDCO vibrational levels in the range of E_v up to $\sim 10000 \text{ cm}^{-1}$ (and even higher), using the MLT PES [17], and to compare our results with the recent experimentally measured values [38]. We perform detailed assignments of all our calculated energies up to $E_v \sim 5000 \text{ cm}^{-1}$ and of a selection of energies in the higher energy range up to $E_v \sim 10000 \text{ cm}^{-1}$ (including all experimentally measured frequencies in [38]) and compare our assignments with the assignments by Ellsworth et al. [38], based on their experimental spectroscopic measurements that were fitted to a multiresonant Hamiltonian model. Some assignments have been changed in this work compared to our recent work [39], as a result of the more extensive calculations performed here.

This work is organized as follows. In Section 2 we give a brief description of the technical features of our method (vibrational coordinates and Hamiltonian, vibrational basis set, search/selection algorithm and Lanczos iteration), that has been described in greater detail in our recent work on formaldehyde H_2CO [28]. Next, in Section 3 we describe the results from our calculations on the HDCO vibrational levels, in the range up to $E_v \sim 10000 \text{ cm}^{-1}$. We supply a list of all S_0 HDCO vibrational states in this energy range, corresponding to the employed PES [17]. We also present and discuss our assignments of some of the calculated vibrational states (mostly in the lower E_v range) and compare them with the frequencies and assignments by Ellsworth et al. [38]. A large number of additional vibrational levels have been calculated and assigned here, that were not observed by Ellsworth et al. [38] and a large number of their assignments have been changed and many new resonances discovered. Section 4 contains our conclusions from the results of the calculations.

2. Vibrational Hamiltonian, basis set functions, search/selection procedure and Lanczos iteration

In our calculations we use the explicit expression of Handy for the kinetic energy of formaldehyde [13], in terms of his curvilinear coordinates q_k (three bond stretches, two interbond angles and one dihedral “book” angle [13]). For the PES of S_0 formaldehyde, we use the original ab initio MLT quartic field [17]. Our 6D basis functions are products of 6 1D basis functions, $\Psi_i = \prod \chi_{nk}(q_k)$. Alternatively in state space, we denote the basis functions as

$$|n_1, n_2, n_3, n_4, n_5, n_6\rangle, \quad (1)$$

where n_k are the excitation quantum numbers for the six vibrational modes. Although we use here local vibrational modes of HDCO (whose shapes are displayed schematically in Fig. 1), they are numbered in closest possible resemblance to the conventional normal mode scheme used for HDCO (as described in Fig. 1 from Ref. [38]). Our local mode basis functions are chosen to resemble most closely the lower excited molecular vibrational eigenfunctions so that the nondiagonal Hamiltonian matrix elements could be as

small as possible. For the three stretching coordinates of the C–D, C–O and C–H bonds, we employ Morse oscillator eigenfunctions $\chi_{nk}(q_k)$, $k = 1, 2, 5$, $n_k = 0, 1, \dots, n_{k0}$ that are optimally adapted to the relevant molecular motions, by setting appropriately the two parameter values of the Morse oscillators. For the out of plane bend, we employ harmonic oscillator eigenfunctions $\chi_{n4}(q_4)$ [$q_4 = \phi$ – the out-of-plane bend (“book”) angle [13,17]]. Finally, for the O–C–H(θ_1) and O–C–D(θ_2) bends (coordinates $q_3 = \cos\theta_1$, $q_6 = \cos\theta_2$), where the molecular configuration did not allow the employment of a harmonic oscillator basis, we use a set of normalized associated Legendre polynomials $P_n^2(\cos\theta)$, $n = 2, 3, \dots$, that cancel the singularities in the kinetic energy operator. However since they have no free parameters to adjust and are not well adapted to the molecular vibrations, for each bend we apply a prediagonalization of the 1D basis (using a simple 1D Hamiltonian) in order to obtain suitable 1D basis functions as linear combinations of the original wavefunctions. This procedure that serves to substantially reduce the number of basis functions required for a vibrational calculation was described in detail in our previous work [28].

Our specific search/selection procedure for constructing the Hamiltonian matrix H in a vibrational calculation, involves the intermediate calculation of a great number of Hamiltonian matrix elements (that are employed to test whether a state should be selected or not), greatly exceeding the final number of elements in H . Therefore we need a very fast method for calculation of matrix elements that does not include numerical integrations. For this purpose, prior to each actual vibrational calculation, we compute a number of required 2D arrays $P_{m_i, n_i}^{l_i, q_i} = \langle \chi_{m_i}(q_i) | F^{q_i}(q_i) | \chi_{n_i}(q_i) \rangle$, $m_i, n_i = 0, 1, 2, \dots, n_{i0}$, corresponding to each one of the vibrational coordinates q_i and to each function or operator $F^{q_i}(q_i)$, occurring in either kinetic energy or PES expressions, using either Gauss–Hermite, Gauss–Laguerre or Gauss–Legendre numerical integrations [40], where n_{i0} is the number of basis functions employed for the vibrational coordinate q_i . All computed $n_{i0} \times n_{i0}$ arrays are stored in computer core memory, ready to use in the subsequent matrix elements calculations. As a result of this and of the separable forms of the employed kinetic energy and PES expressions, each matrix element is obtained as the sum of products of the appropriate $P_{m,n}^{l,q}$ values, thus reducing the actual calculation to a number of multiplications and summations and no integrations, which greatly accelerates the calculation of matrix elements.

Our search/selection procedure serves to select an optimally small however representative active space of basis states, that are involved in the vibrational calculation, from a huge primitive space of basis states, originally available. The search/selection procedure employed here, described in detail in our work [28], is similar to the artificial intelligence based techniques, developed

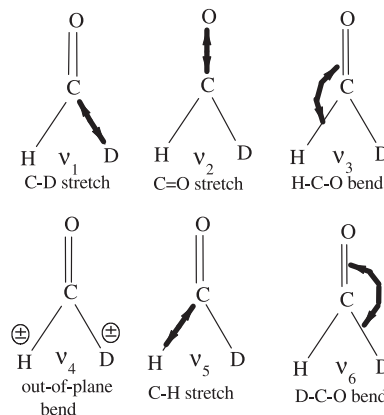


Fig. 1. Six vibrational curvilinear coordinates and local modes, used as basis states in the vibrational description of HDCO.

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