Ab Initio Calculation of the Low-Lying Vibrational States of $C_2H_2(\tilde{A})$ in Full Dimensionality

Jaime Rheinecker and Joel M. Bowman*

Cherry L. Emerson Center of Scientific Computation and Department of Chemistry, Emory University, Atlanta, Georgia 30322

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We report full-dimensional calculations of vibrational energies of *trans*-$C_2H_2(\tilde{A})$ using the code MULTIMODE and with a full-dimensional potential energy surface obtained by fitting singles and doubles coupled-cluster equations-of-motion (EOM-CCSD) energies using a [3s 2p 1d] atomic natural orbital basis. The EOM-CCSD calculations were done with the code "ACES II". We compare the properties of the potential surface to previous calculations at the trans minimum and also compare the vibrational energies to experimental ones.

I. Introduction

The spectroscopy of the first excited singlet state of acetylene has been of intense interest for a number of years and for a variety of reasons. Part of this interest stems form the fact that unlike the ground electronic state C_2H_2 is bent in the Ã state, with two minima corresponding to trans and cis configurations (trans is the lower energy minimum) and, in addition, the dissociation energy is quite low, i.e., of the order of four thousand wavenumbers. Most relevant to this paper are experiments by Crim and co-workers[1] and recent ones of Field and co-workers,[2] who have probed the low-lying vibrational states of C_2H_2 (hereafter we will drop the electronic state label and use S_1 instead). A further interesting possible "complication" of the dynamics in the S_1 state is a conical intersection with S_2. This has been explored in considerable detail theoretically.[3−5] Intersections between S_1 and triplet states have also been studied theoretically in the context of photodissociation.[3,6,7] These intersystem crossings do not take place in the region of the low-lying vibrational states of *trans*-C_2H_2; however, the S_1−S_2 nonadiabatic interactions may play some role in this region. Nonetheless, vibronic coupling is not considered here. It should also be noted that in the linear geometry the S_1 state is $^1\Sigma_u^-$.

Another motivation for studying the vibrational states of *trans*-C_2H_2 is the proposal by Field and Jacobson[8] that stimulated emission pumping to S_0 from these states may populate the high-energy vinylidene isomer of S_0-acetylene.[9,10]

Experimental work on the spectrum of S_1-C_2H_2 was reported by Crim and co-workers in the early 1990s.[1] They reported the rovibrational energies of the six fundamentals by vibrational overtone excitation combined with laser-induced fluorescence detection. In new experimental work in 2003 the symmetric CH stretching frequency was revised from 3040 cm^{-1} to a lower value of 2880 cm^{-1} by Field and co-workers.[2] In that paper Stanton provided some theoretical support for this new assignment by calculating quartic force constants using the EOM-CCSD approach.

Ab initio geometry optimizations and single point energy calculations of S_1-C_2H_2 have been performed by Stanton using EOM-CCSD/TZ2P calculations.[11,12] These were followed by two studies of the portions of the potential relevant to photodissociation using CASPT2/PVTZ//EOM-CCSD/DZP,[3] and CASSCF/DZP calculations[6] to obtain geometries, energies, and normal modes, In 1998 Hohlneicher published stationary point geometries and vertical excitation energies using CASPT2//CASSCF and CASPT2 calculations.[13] Lischka has reported a multireference CI investigation of stationary points of several potential energy surfaces and surface crossings.[4,14,15]

To describe the vibrational states of C_2H_2 and to investigate the Field−Jacobson proposal, the use of a variational method with a full-dimensional potential energy is needed. We aspire to develop such a potential; however, here we report a portion of that potential, i.e., the region of the trans minimum. We use this potential to perform variational calculations using the code MULTIMODE.[16]

This paper is organized as follows. Section II describes the theoretical methods and calculations used in the development and analysis of the surface as well as parameters for our calculations. Section III provides our results and a discussion of our results and how they compare to previous theoretical and experimental studies. We briefly summarize the study and give concluding remarks in section IV.

II. Calculations

S_1 Potential Energy Surface (PES). To obtain a PES we used the approach adopted in our group over the past several years, beginning with a PES for S_0-C_2H_2.[9,10] In this approach we fit ca. 10 000 ab initio energies to a global functional form in terms of the internuclear distances. For the present purpose, i.e., a PES localized in the *trans*-region of S_1-C_2H_2, we proceeded as follows. We first perform a normal-mode analysis at the optimized trans geometry of acetylene to get the matrix of eigenvectors, **C**, which relates the mass-weighted Cartesian coordinate displacements **q** to the normal mode displacements **Q** by the usual expression (eq 1).

$$\mathbf{q} = \mathbf{C}\mathbf{Q} \tag{1}$$

The six vibrational normal modes of the S_1 trans geometry, along with one-dimensional cuts of the potential along these modes are shown in Figure 1.

The grids for our potential energy surface were generated by varying the vibrational normal modes according to the *n*-mode

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* Corresponding author. E-mail address: jmbowma@emory.edu.

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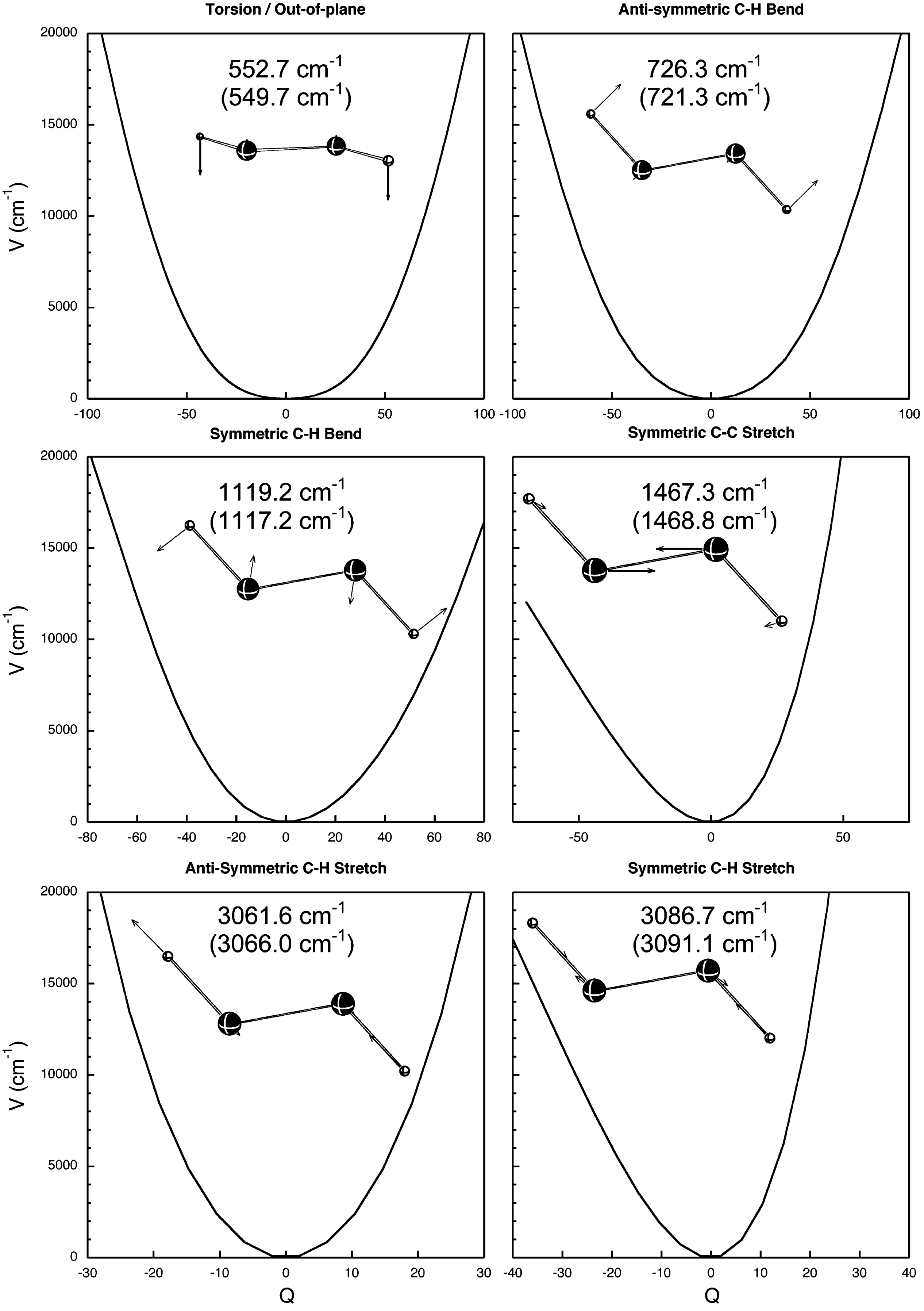

Figure 1. 1-D cuts of trans S_1 normal modes from our surface with corresponding vibrational displacement figures and ab initio harmonic frequencies inset with PES frequencies in parentheses.

TABLE 1: Comparison of Optimized *trans*-$C_2H_2(\tilde{A})$ Geometries from ab Initio and PES, in Parentheses, with Previous Results, Where Values Are in Units of Angstrom and Degrees

	EOM-CCSD/[3s 2p 1d]	other
R_{CH}	1.102 (1.096)	1.091,[a] 1.105,[b] 1.128,[c] 1.109,[d] 1.094,[e] 1.087,[f] 1.092[g]
R_{CC}	1.373 (1.360)	1.36,[a] 1.377,[b] 1.402,[c] 1.389,[d]1.382,[e] 1.367,[f] 1.372[g]
∠CCH	122.3 (123.2)	123.6,[a] 120,[d] 122,[e] 122.8,[f] 122.2[g]

[a] Reference 11, EOM-CCSD/TZ2P. [b] Reference 3, CASPT2/PVTZ//EOM-CCSD/DZP. [c] Reference 6, CASSCK/DZP. [d] Reference 13, CASPT2//CASSCF. [e] Reference 13, CASPT2. [f] Reference 4, MR-CISD/QZP. [g] Reference 4, MR-AQCC/QZP.

representation of the potential.[16] We used a four-mode representation here. As an example of this procedure consider two-mode grids. These were generated by varying all two-mode combinations keeping the remaining four modes fixed at zero. We chose the range of each grid coordinate according to a maximum energy. So, for the one-mode grids the *Q*s ranged from very negative to very positive values to sufficiently cover a large energy range. We then used a tighter grid of points in the lower energy region. We continued to obtain points over smaller displacement ranges with tighter grids until we had a good representation of the surface along any given cut. At the end of this process, we had 2248, 11254, 25411, and 3901 points for the one-, two-, three-, and four-mode coupling grids, respectively, for a total of 42 814 points.

From the normal coordinate configurations we made the standard transformation to obtain the Cartesian coordinates of each atom. We performed a simple geometric test to remove any points that are in the *cis*-bent well. We then used ACES II[17] to perform the EOM-CCSD ab initio energy calculations with the NASA Ames ANO/[3s 2p 1d] (DZP) basis set[18] with the use of spherical harmonics for the d-functions. The ANO method was chosen due to the recommendation presented by Martin et al. for accurate frequency calculations on unsaturated systems.[19] Then we further reduced our data set to contain only data points with energies of less than or equal to 22 000 cm^{-1} and were left with 22 334 data points.

This data set of energies was fit by least squares to get the coefficients using the functional form and definition of internuclear distances used previously for S_0-C_2H_2,[10] namely

$$V(r_1,r_2,r_3,r_4,r_5,r_6) = \sum_{n_1+n_2\ldots\leq 5} C_{n_1\ldots n_6} y_1^{\,n_1} \ldots y_6^{\,n_6}$$

$$y_i = [1 - e^{-\alpha(r_i - r_{i,\mathrm{eq}})}] \tag{2}$$

where y_i is the Morse variable, $r_{i,\mathrm{eq}}$ is the value of a given bond length at the trans-equilibrium geometry, and α is set to 0.5. In the present case the surface was developed with a total order, i.e., sum of the six integers, less than or equal to 5. This resulted in a total of 462 coefficients, $C_{n_1\ldots\ n_6}$, which were determined using a standard least-squares/singular value decomposition procedure.

Vibrational Calculations. The vibrational calculations were done using MULTIMODE,[15] version 5.2 (MM52). This code does vibrational self-consistent field (VSCF) and several types of configuration interaction (CI) calculations for the rovibrational energies and wave functions of polyatomic molecules, transition states, clusters, etc. The code is based on the Watson Hamiltonian and can currently include potential coupling of up to five modes.

We systematically varied several parameters within this code including n-mode potential coupling, Coriolis coupling, basis set coupling, and basis size until convergence is reached. For example, we varied potential coupling and basis set coupling each from 3 to 5, independently, and compared the zero point energies as well as fundamentals. While there were differences of more than 10 cm^{-1} between three- and four-mode coupling the results for four- and five-mode coupling were very similar and were determined to be converged. Our final results were calculated with five-mode potential coupling, three-mode Coriolis coupling, and five-mode basis coupling. Using C_{2h} symmetry, the CI matrix sizes were 5478, 5172, 3310, and 3512 for the four symmetry blocks.

III. Results and Discussion

S_1 Potential Energy Surface. Our new potential energy surface (PES) is full-dimensional but local to the trans region of the first excited state of acetylene. Table 1 gives results of direct ab initio geometry optimization for the trans minimum, the geometry optimized on the PES (in parentheses) and comparisons with previous results from other groups. The PES geometry agrees well with the direct ab initio one, and both agree well with previous results. Normal-mode frequencies obtained both directly from ab initio calculations and from the PES are given in Figure 1. The frequencies for the in-plane modes are similar to previous calculations;[1,4,11,12] however, our out-of-plane harmonic frequency is much lower than obtained with higher-level calculations. This difference was noted previously.[12] For example this frequency changed from 506 to 615 cm^{-1} in going from a DZP basis (the one used here) to a TZP basis and using the EOM-CCSD method.[12] On the basis of this significant underestimation of the harmonic frequency at the [3s 2p 1d] level, we can anticipate an underestimation of the anharmonic/coupled vibrational frequency obtained with MULTIMODE. Also, it should be noted that inclusion of f-functions has previously been shown to be important for ground-state acetylene[20] and may also be important for the excited state, although we have not examined that here.

The root-mean-square (RMS) fitting error of the PES was calculated at various energy ranges such that all energies below a given cutoff energy are used in the calculation of the RMS. These results are presented in Figure 2. Although the PES is not global, i.e., does not dissociate correctly, it does not diverge in the limit R_{CH} goes to infinity as it is fit with Morse variables. The small RMS and the accurate normal-mode frequencies relative to the direct ab initio ones show that our fit is a very good representation of the ab initio data.

Vibrational Frequencies. The calculated vibrational frequencies are presented in Table 2 and compared with experiment. Our fundamental frequencies agree reasonably well with experiment for all in-plane vibrations. It is especially noteworthy that the calculated frequencies are significantly lower than the harmonic ones for modes 3, 2, 4, and 1 (and in much better agreement with experiment than the harmonic ones). However, the calculated energy for 6^1 is roughly 200 cm^{-1} below experiment. This result is not unexpected given the discussion above, which concluded, based on previous numerical tests of harmonic frequencies, that the [3s 2p 1d] basis is inadequate for this mode. However, the difference with experiment is roughly twice the difference in the harmonic frequency between the [3s 2p 1d] and TZP basis.

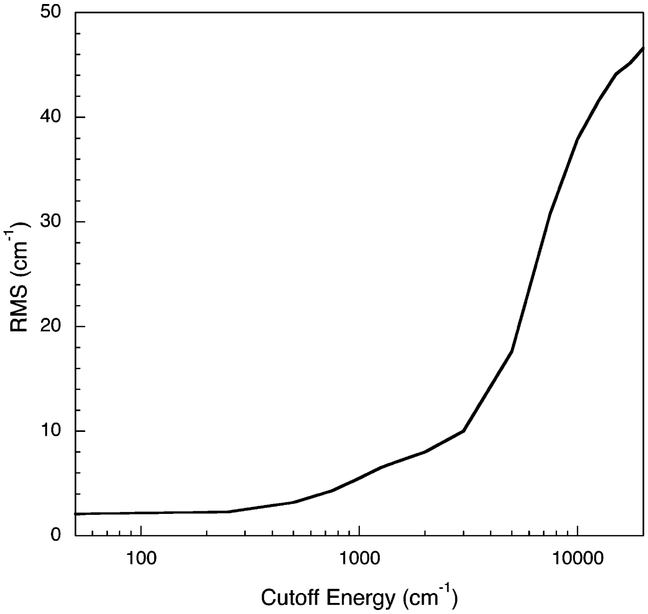

Figure 2. Semilog plot of RMS values with respect to cutoff energies, in wavenumbers, for our least-squares fit of the trans S_1 potential energy surface.

TABLE 2: Comparison of Present Calculated and Experimental Vibrational Energies in cm^{-1} for the Indicated States

vibrational mode	state assignment	calculated	experiment
torsion/out-of-plane	6^1	553.8	764.9[a] 735[b]
antisymmetric C−H bend	4^1	703.69	768.3[a] 768[b]
trans C−H bend	3^1	1008.83	1047.55[a] 1047.72[d]
symmetric C−C stretch	2^1	1395.4	1386.9[a] 1387.28[d]
antisymmetric C−H stretch	5^1	2884.48	2857.4[a]
symmetric C−H stretch	1^1	2903.28	2880.5[c]
	3^12^2	3821.1[e]	3798[c]
	3^11^1	3897.65	3917[c]
	3^2	2022.19	2077.69[d]
	3^12^1	2377.66	2405.16[d]
	3^3	3041.29	3088.31[d]
	3^22^1	3387.22	3465.78[d]
	3^4	4062.76	4073.93[d]
	3^32^1	4420.56	4476.40[d]

[a] Reference 1. [b] Reference 22. [c] Reference 2. [d] Reference 21. [e] Mixed state, see text for discussion.

The present calculations are also in agreement with the reassignment by Merer et al.[2] of the symmetric C−H stretch as well as with the combination bands that were described in that paper. In the latter case we did find two states with dominant 2^23^1 character, the one with a slightly higher leading "CI" coefficient for this state is listed in the table and is in good agreement with the experimental assignment. The other mixed state 2^23^1 character has an energy of 3952.1 cm^{-1}. Both states are mixed with an overtone of the torsion. The other combination band is the 1^13^1 state and the calculated energy is within 20 cm^{-1} of the experimental energy.[2]

Finally, in Table 2, we also included some older experimental results for overtone and combination states[21] for comparison with which we show very good agreement.

IV. Summary and Conclusions

A full-dimensional potential energy surface describing the trans-bent region of the S_1 state of C_2H_2, based on fitting roughly 22 000 EOM-CCSD/[3s 2p 1d] electronic energies, has been reported and characterized. Full dimensional vibrational energies were calculated with this potential using the code MULTIMODE. There is good agreement with experiment for the fundamentals and combinations bands of the in-plane modes. Agreement is poor for the fundamental of the out-of-plane torsional mode. It appears that a large part of the source of this error is the basis set used; however, possible interaction with the S_2 state (for which a conical intersection is known for nonplanar geometries is known) may also be a source of error as well. Thus, theoretical studies of excitation of the to out-of-plane torsion clearly need more study.

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