An ab initio calculation of v1 and v3 for triplet methylene (3B1CH2) and the determination of the vibrationless singlet–triplet splitting Te(1A1)

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An *ab initio* calculation of ν_1 and ν_3 for triplet methylene ($\tilde{X}\,^3B_1$ CH$_2$) and the determination of the vibrationless singlet–triplet splitting $T_e(\tilde{a}\,^1A_1)$

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Ab initio values of ν_1, ν_3 and the zero point energy for triplet methylene ($\tilde{X}\,^3B_1$ CH$_2$) have been calculated. Complete second order configuration interaction calculations for the six valence electrons, with a Davidson-type unlinked cluster correction, were done at 37 selected nuclear geometries. We have fitted an analytic potential through these points and used the nonrigid bender Hamiltonian, and a variational procedure, to calculate the rotation–vibration energies. We have obtained $\nu_1 = 2985 \pm 20$ cm^{-1}, $\nu_3 = 3205 \pm 20$ cm^{-1}, and the zero point energy as 3710 ± 20 cm^{-1}. The uncertainties represent our best estimate of the full uncertainties in the calculations. From the experimental data for singlet methylene ($\tilde{a}\,^1A_1$) we have determined the zero point energy of that state to be 3620 ± 20 cm^{-1}. Combining these two zero point energies with the experimental value of $T_0(\tilde{a}\,^1A_1) = 3156 \pm 5$ cm^{-1} [Bunker *et al.*, J. Chem. Phys. **85**, 3724 (1986)] we obtain the vibrationless singlet–triplet splitting $T_e(\tilde{a}\,^1A_1) = 3246 \pm 30$ cm^{-1} (9.28 ± 0.1 kcal/mol).

I. INTRODUCTION

Since the detection of the infrared spectrum of gas phase triplet methylene ($\tilde{X}\,^3B_1$ CH$_2$) by Sears, Bunker, and McKellar[1] in 1981 much infrared spectroscopic data has been obtained and analyzed for this species (see Refs. 2 and 3 and references therein). However, the two stretching fundamental bands have not yet been detected, presumably because they are very weak,[4] and the values of ν_1 and ν_3 remain unknown. It is important to know the values of ν_1 and ν_3 so that the rotational levels of the $v_1 = 1$ and $v_3 = 1$ states can be precisely located, and thus the perturbing effect of these levels on the singlet state ($\tilde{a}\,^1A_1$) levels analyzed. Also, knowledge of ν_1 and ν_3 would allow the zero point energy of triplet methylene to be determined and hence the vibrationless singlet–triplet splitting $T_e(\tilde{a}\,^1A_1)$ could be obtained from the known experimental value[3] of $T_0(\tilde{a}\,^1A_1) = 3156 \pm 5$ cm^{-1}.

In this paper we report the results of an *ab initio* calculation of ν_1 and ν_3 for triplet methylene, and we hope that this will be of assistance in the experimental search for these fundamental bands. We have fitted an analytic expression to 37 points on a potential energy surface computed from a complete second order configuration interaction wave function (SOCI) for the six valence electrons, with a Davidson-type unlinked cluster correction[5] (SOCI + Dav) included. Using the nonrigid bender Hamiltonian[6] (NRB2), and a variational procedure[7] (JGEOS), to calculate vibrational frequencies with this potential function we have obtained

$\nu_1 = 2985$, $\nu_2 = 967$, and $\nu_3 = 3205$ cm^{-1} (the experimental value[2] of ν_2 is 963.10 cm^{-1}). For the $\tilde{a}\,^1A_1$ singlet state we know $\nu_1 = 2805.9$ cm^{-1}, $\nu_2 = 1352.6$, and $\nu_3 = 2864.5$ cm^{-1} from experiment.[8,9] The zero point energies of the triplet (*ab initio*) and singlet (experimental) states are obtained as 3710 ± 20 and 3620 ± 20 cm^{-1} respectively, and, hence, we determine $T_e(\tilde{a}\,^1A_1) = 3246 \pm 30$ cm^{-1} (9.28 ± 0.1 kcal/mol).

II. THE *AB INITIO* CALCULATION

The results of the *ab initio* calculation of the potential energy surface of triplet methylene ($\tilde{X}\,^3B_1$ CH$_2$) are given in Table I. Two potential energy surfaces are tabulated. The one labeled SOCI is from a variational configuration interaction calculation in the configuration space

C(1s)	C(2s)C(2p_x)C(2p_y)C(2p_z)H$_1$(1s)H$_2$(1s)	X
2	6	0
2	5	1
2	4	2

made up from a zeroth order space [zero electrons in the external orbitals (X)], a first order space (one electron in X), and a second order space (two electrons in X). In each of these spaces two electrons occupy the core C(1s) orbital and the remaining electrons, six in the zeroth order space, five in the first order space, and four in the second order space, are distributed in all possible ways among the strongly occupied valence orbitals shown. The core and valence orbitals make up the internal orbitals. The internal orbitals are optimum expansions, in a chosen set of basis functions, determined to minimize the energy of the lowest Hamiltonian eigenvector

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in the zeroth order configuration space. The external orbitals span the orthogonal complement of the internal orbitals in the space of the basis set. In common computational terminology the internal orbitals are described as CASSCF (complete active space self consistent field) orbitals, and the wave function as a complete six electron SOCI (second order configuration interaction) wave function. If the basis set is near complete for internal orbital expansion, this potential energy surface will be very close to the true one. A computational error remains due to the fact that the SOCI expansion only approximates a complete CI expansion; other errors are due to neglect of core–valence electron correlations, and to a lesser extent from neglect of core–core electron correlations and relativistic effects. We have used two basis sets for orbital expansions. In the first, four s-, three p-, two d-, and one f-type contracted Gaussian functions are centered on carbon, and three s-, and one p-type functions on each of the hydrogen atoms. In the second, used in the results presented in Table I, a second p function is added to each hydrogen. As will be discussed in the next section, the second basis is needed to improve our computed equilibrium CH bond length; comparison of results from the two basis sets lends confi-

dence to our error bars. These "medium" sized basis sets are as large as is practical for most calculations (the dimension of our SOCI configuration space is 177815). In this particular case our results can be calibrated against "large" basis set calculations, near the complete basis limit, done recently by Bauschlicher, Langhoff, and Taylor (BLT)[10] to refine the purely *ab initio* computation of the chemically and historically important vibrationless singlet–triplet splitting in CH_2. The second potential surface of Table I, labeled SOCI + Dav, contains an empirical adjustment which partially corrects the shape of the SOCI surface towards that of a complete CI. All results reported here are with this surface; analysis of the uncorrected surfaces is incorporated into our error bars. We conclude that the *ab initio* calculations contribute an uncertainty, at the most, of ± 10 cm^{-1} to the calculation of ν_1 and ν_3.

To calculate rotation–vibration energies from the 37 *ab initio* points it is necessary to use an analytic expression for the shape of the potential where we adjust the parameters in the expression so that it fits the *ab initio* points. We have used the same type of analytic expression as used in Eqs. (1) and (2) of Ref. 3, and this is given by

TABLE I. The *ab initio* values of the potential energy surface for the $\tilde{X}\,{}^3B_1$ state of methylene.

$r_{12}/\text{Å}$	$r_{23}/\text{Å}$	α/deg	*Ab initio* energy/hartree		(SOCI + Dav)-fitted $(10^{-6}$ hartree)
			SOCI	SOCI + Dav	
1.084	1.084	134	− 39.071 177	− 39.075 133	− 1
1.164	1.164	134	− 39.063 581	− 39.067 620	− 80
1.224	1.224	134	− 39.050 954	− 39.055 050	1
1.014	1.014	134	− 39.064 560	− 39.068 440	35
0.974	0.974	134	− 39.052 832	− 39.056 668	− 18
0.974	1.224	134	− 39.051 226	− 39.055 185	− 14
1.014	1.164	134	− 39.063 833	− 39.067 793	− 30
1.084	1.084	90	− 39.036 289	− 39.040 088	0
1.084	1.084	110	− 39.062 226	− 39.066 094	66
1.084	1.084	130	− 39.071 001	− 39.074 944	− 18
1.084	1.084	140	− 39.070 693	− 39.074 671	19
1.084	1.084	160	− 39.065 340	− 39.069 387	− 16
1.084	1.084	180	− 39.061 626	− 39.065 698	18
0.950	0.950	134	− 39.042 249	− 39.046 058	− 46
1.064	1.064	134	− 39.070 802	− 39.074 737	26
1.074	1.074	134	− 39.071 124	− 39.075 070	13
1.094	1.094	134	− 39.070 974	− 39.074 942	− 17
1.254	1.254	134	− 39.043 121	− 39.047 244	56
1.014	1.014	180	− 39.057 107	− 39.061 112	− 6
1.064	1.064	180	− 39.061 828	− 39.065 881	31
1.104	1.104	180	− 39.060 425	− 39.064 518	− 3
1.164	1.164	180	− 39.051 866	− 39.056 019	15
1.140	1.140	180	− 39.056 088	− 39.060 218	− 19
1.120	1.120	180	− 39.058 819	− 39.062 928	− 14
1.100	1.100	180	− 39.060 740	− 39.064 828	3
1.080	1.080	180	− 39.061 750	− 39.065 818	22
0.950	1.254	134	− 39.041 690	− 39.045 645	6
0.974	1.224	110	− 39.043 094	− 39.046 967	− 53
1.014	1.164	110	− 39.055 173	− 39.059 043	− 10
0.974	1.224	180	− 39.040 977	− 39.045 046	− 24
1.014	1.164	180	− 39.054 037	− 39.058 109	− 15
0.935	0.935	134	− 39.034 074	− 39.037 865	− 11
0.920	0.920	134	− 39.024 573	− 39.028 347	36
1.280	1.280	134	− 39.035 720	− 39.039 864	64
1.310	1.310	134	− 39.026 619	− 39.030 787	− 68
0.935	1.280	134	− 39.033 607	− 39.037 561	36
0.925	1.305	134	− 39.026 459	− 39.030 413	15

$$V(\bar{\rho}, r_{12}, r_{23}) = V_e + V_0(\bar{\rho}) + \tfrac{1}{2}f_{rr}(\Delta r_{12}^2 + \Delta r_{23}^2) + f_{rr'}\Delta r_{12}\Delta r_{23} + f_{r\alpha}(\Delta r_{12} + \Delta r_{23})\Delta\alpha$$

$$+ \tfrac{1}{2}f_{r\alpha\alpha}(\Delta r_{12} + \Delta r_{23})\Delta\alpha^2 + f_{rr'\alpha}\Delta r_{12}\Delta r_{23}\Delta\alpha + \tfrac{1}{6}f_{rrr}(\Delta r_{12}^3 + \Delta r_{23}^3)$$

$$+ \tfrac{1}{24}f_{rrrr}(\Delta r_{12}^4 + \Delta r_{23}^4) + \tfrac{1}{2}f_{rr'\alpha\alpha}\Delta r_{12}\Delta r_{23}\Delta\alpha^2, \tag{1}$$

where

$$V_0(\bar{\rho}) = \frac{H(1 + c\bar{\rho}^2)f_{\alpha\alpha}(\bar{\rho}^2 - \rho_e^2)^2}{f_{\alpha\alpha}\rho_e^4 + [8H(1 + c\bar{\rho}^2) - f_{\alpha\alpha}\rho_e^2]\bar{\rho}^2}. \tag{2}$$

In these expressions V_e is the energy at the minimum, $\Delta r_{12} = r_{12} - r_e$, $\Delta r_{23} = r_{23} - r_e$, $\Delta\alpha = \alpha - \alpha_e$, r_{12}, and r_{23} are the instantaneous values of the two bond lengths, r_e is the equilibrium value, $\bar{\rho}$ is the instantaneous value of the supplement of the bond angle ($\bar{\rho} = \pi - \alpha$), and ρ_e is the equilibrium value ($\rho_e = \pi - \alpha_e$). The bending potential $V_0(\bar{\rho})$ given in Eq. (2) is the bending potential for $r_{12} = r_{23} = r_e$ fixed, and it involves four parameters, which are H the height of the barrier to linearity in V_0, ρ_e the equilibrium angle, $f_{\alpha\alpha}$ the harmonic bending force constant at $\bar{\rho} = \rho_e$, and c which allows the anharmonicity around ρ_e to be adjusted. Including r_e and V_e, this expression for $V(\bar{\rho}, r_{12}, r_{23})$ involves 14 adjustable parameters, but $f_{r\alpha\alpha}$ and $f_{rr'\alpha\alpha}$ are constrained by the symmetry required about linearity (see footnote b in Table II).

The 37 nuclear geometries were chosen to give a good coverage of the potential up to about 10 000 cm^{-1} above equilibrium. The standard deviation of the fitting was 8.7 cm^{-1} and the deviations are given in the last column of Table I. No significant improvement in the fitting was obtained by including more terms in the expression for V. The values of the parameters obtained from this fitting are given in Table II.

III. THE ROTATION–VIBRATION CALCULATION

We have calculated rotation–vibration energies for triplet methylene with the nonrigid bender Hamiltonian[6]

(NRB2), and with the variational program[7] JGEOS, using the potential function of Eqs. (1) and (2) with the parameter values as in Table II. The mean results are given for CH$_2$ and CD$_2$ in Table III, and a comparison with experiment is included. We have also included the calculated zero point energies in this Table. Using the nonrigid bender and variational Hamiltonians with fitted potential functions containing more force constants leads us to the conclusion that there is an uncertainty of ± 10 cm^{-1} in the calculation of ν_1 and ν_3, in addition to the uncertainty of ± 10 cm^{-1} coming from the *ab initio* calculation; thus, the uncertainties in ν_1 and ν_3 for CH$_2$ are ± 20 cm^{-1} and the uncertainty in the zero point energy is ± 20 cm^{-1}. For CD$_2$ the uncertainties in ν_1 and ν_3 are ± 10 cm^{-1}. We encourage experimentalists to search for the ν_1 band of CD$_2$ for which the transition moment (0.006 D from the results of Ref. 4; compare with the rotation-bending transition moments in Table V of Ref. 4) is the highest, for which our predicted frequency (2157 cm^{-1}) has a small uncertainty (± 10 cm^{-1}), and for which there will be no complications from singlet–triplet perturbations.

In order to make a comparable calculation of the zero point energy for the $\tilde{a}$ $^1A_1$ state we have used the nonrigid bender Hamiltonian to fit the experimental vibrational energies.[8,9,12] In this calculation for the well bent singlet state we have used the expression given in Eq. (1) above for the internuclear potential, with a standard Taylor series expansion of $V_0(\rho)$ about equilibrium rather than the expression given in Eq. (2) above which is appropriate for a quasilinear state. The zero point energies obtained in this calculation are 3620 cm^{-1} for CH$_2$ and 2675 cm^{-1} for CD$_2$. By refitting the data varying different force constants we determine the uncertainty of these quantities to be ± 20 cm^{-1}.

IV. DISCUSSION

In this paper we have calculated an *ab initio* potential surface for $\tilde{X}$ $^3B_1$ methylene and this is given in Tables I and II [see Eqs. (1) and (2)]. Using this potential surface and the nonrigid bender Hamiltonian[6] (NRB2), and the vari-

TABLE II. Values of parameters derived from fitting to the SOCI + Dav *ab initio* points in Table I. See Eqs. (1) and (2) for the definitions of the parameters.

V_e/hartree	− 39.075 144(14)[a]
r_e/Å	1.080 81(11)
α_e/deg	134.08(12)
H/cm^{-1}	2046.9(39)
$f_{\alpha\alpha}$/mdyn Å	0.366 5(28)
c	− 0.042 6(49)
f_{rr}/mdyn Å^{-1}	5.770 7(72)
$f_{rr'}$/mdyn Å^{-1}	− 0.095 0(19)
$f_{r\alpha}$/mdyn	0.151 3(21)
f_{rrr}/mdyn Å^{-2}	− 34.86(19)
$f_{r\alpha\alpha}$/mdyn	− 0.188 8[b]
$f_{rr'\alpha}$/mdyn Å^{-1}	− 0.112(11)
f_{rrrr}/mdyn Å^{-3}	154.7(3.2)
$f_{rr'\alpha\alpha}$/mdyn Å^{-1}	0.140[b]

[a] The number in parentheses is one standard error.
[b] Constrained by symmetry about linearity using $f_{r\alpha\alpha} = -f_{r\alpha}/\rho_e$ and $f_{rr'\alpha\alpha} = -f_{rr'\alpha}/\rho_e$.

TABLE III. Rotation–vibration energies (in cm^{-1}) calculated using the parameters from Table II.

	CH$_2$		CD$_2$	
	calculated	experiment	calculated	experiment
ν_1	2985	···	2157	···
ν_2	967	963.10[a]	754	752.37[b]
ν_3	3205	···	2428	···
$\nu_1 + \nu_2$	3955	···	2909	···
$\nu_2 + \nu_3$	4180	···	3187	···
Zero pt. energy	3710	···	2740	···

[a] Reference 2.
[b] Reference 11.

ational procedure[7] JGEOS, we have calculated $v_1 = 2985 \pm 20$ cm^{-1}, $v_3 = 3205 \pm 20$ cm^{-1}, and the zero point energy as 3710 ± 20 cm^{-1}. By fitting to experimental data[8,9,12] for $\tilde{a}\ {}^1A_1$ methylene, using the nonrigid bender Hamiltonian, we have determined that the zero point energy of the singlet state is 3620 ± 20 cm^{-1}. Combining these zero point energies with the experimental value[3] of $T_0(\tilde{a}\ {}^1A_1) = 3156 \pm 5$ cm^{-1} gives the value $T_e(\tilde{a}\ {}^1A_1) = 3246 \pm 30$ cm^{-1} (9.28 ± 0.10 kcal/mol). The BLT SOCI calculation[10] gives $T_e(\tilde{a}\ {}^1A_1) = 9.22$ kcal/mol which is very satisfactorily consistent with our determination; the singlet–triplet splitting in methylene $T_e(\tilde{a}\ {}^1A_1)$ is at last certain to ± 0.1 kcal/mol.

Some comment is necessary on the differences between the *ab initio* values of the potential surface parameters in Table II here, and the values obtained from an NRB fit to the experimental data given in Table II of Ref. 3. The equilibrium bond length obtained here is 1.081 Å whereas the value obtained from the NRB2 fit[3] to the data is 1.077 Å. The BLT SOCI calculation[10] in a "large" basis gives 1.079 Å, in more satisfactory agreement with the value in Ref. 3. We believe that the values of v_1 and v_3 will not be changed by more than 10 cm^{-1} in a more extended *ab initio* calculation. Our strongest evidence for this is that in our SOCI + Dav calculations with the smaller basis (one less p function on each hydrogen) the values of v_1 and v_3 decrease by only 3 and 2 cm^{-1}, respectively, even though r_e increases, away from the observed value, from 1.081 to 1.084 Å. We conclude that increasing our basis set further, towards the BLT basis which is nearly complete, will not take v_1 and v_3 out of our reported range. The stretching force constants obtained here do not agree very well with those determined in Ref. 3. One possible reason for this discrepancy is that the nonrigid bender treats the effects of centrifugal stretching of the bonds by second order perturbation theory, and if this leads to serious short-

comings then in a fit to data involving high angular momentum states (such as done in Ref. 3) the stretching force constants will adjust themselves away from their true values in order to compensate for this deficiency in the model. If this is true then in the parlance of spectroscopy one would say that the stretching force constants obtained from a nonrigid bender fit to data involving high angular momentum states are "effective" rather than "true." What is true is that the data in Ref. 3 can be fitted well using the NRB2 Hamiltonian even if we include the *ab initio* values obtained here for v_1 and v_3; a similar good fit can be obtained if these frequencies are taken to be as high as 3300 cm^{-1}. Clearly with only the available experimental data to hand we cannot determine v_1 or v_3 reliably; this is the motivation behind our *ab initio* calculation of them.

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