THE PREDISSOCIATION OF THE $\tilde{d}\ ^1A_2$-STATE OF METHYLENE: A COMBINED *AB INITIO* (MRCI) AND VARIATIONAL (TROVE) STUDY

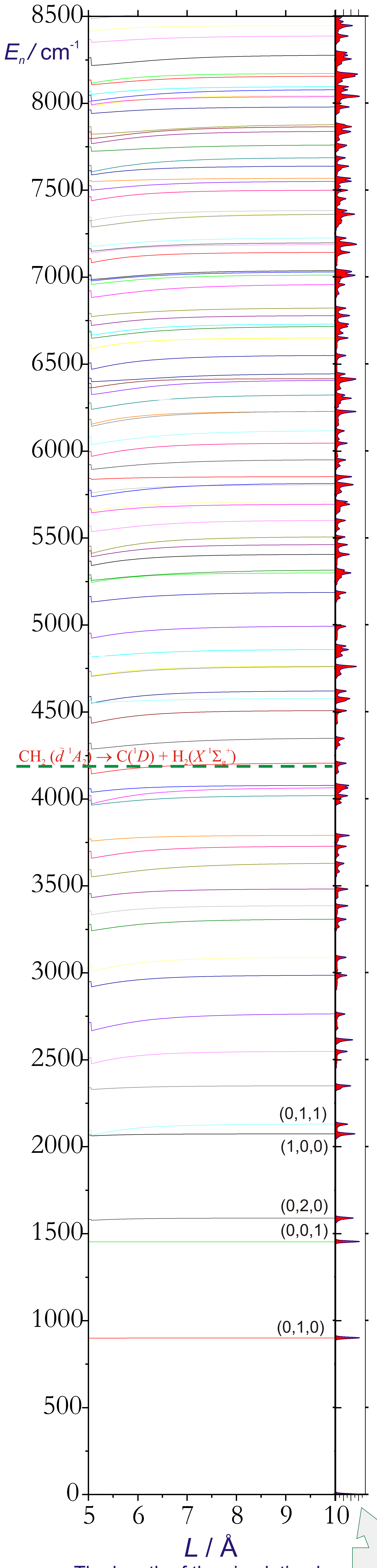
Sergei N. Yurchenko
Physikalische Chemie,
TU Dresden, Germany

Bojana Ostojić
Institute of Chemistry,
University of Belgrade,
Serbia

Per Jensen
FB C - Theoretische
Chemie, Bergische
Universität Wuppertal,
Germany

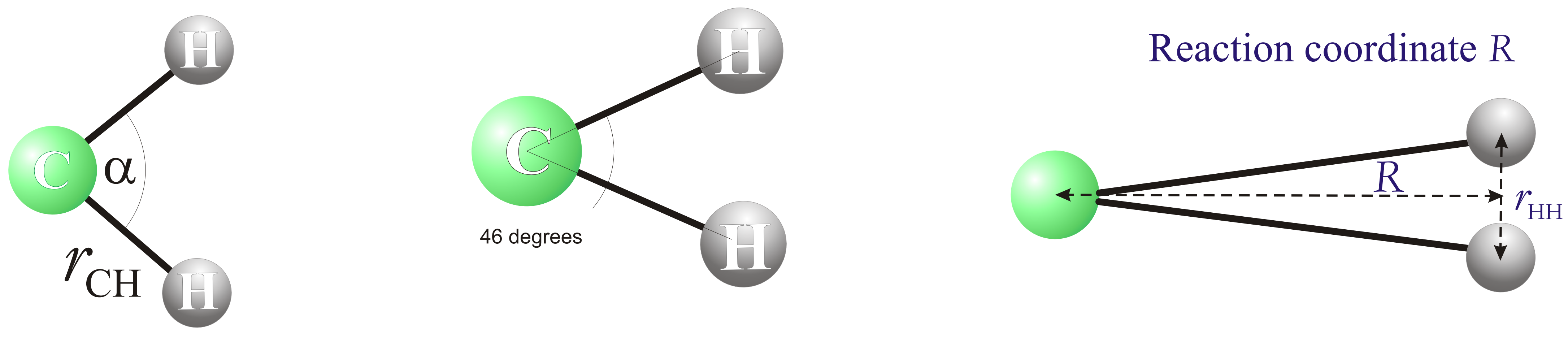
Philip R. Bunker
Steacie Institute for
Molecular Sciences,
NRC of Canada,
Ottawa, Canada

Resonances*: Vibrational term values for* $\tilde{d}\ ^1A_2$-state CH_2 as a function of the size of the simulation box *L (Å)*.

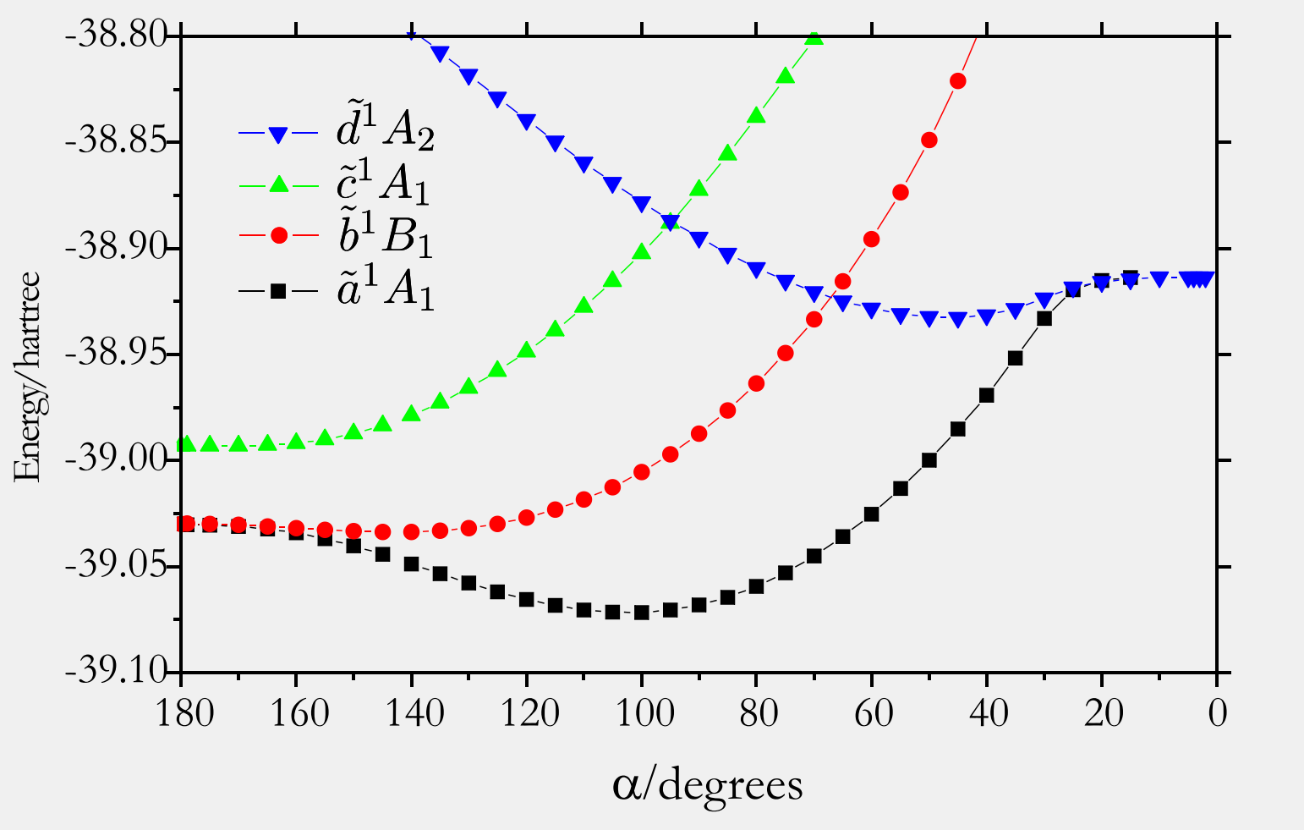


The length of the simulation box along the coordinate *R*(C-H_2)

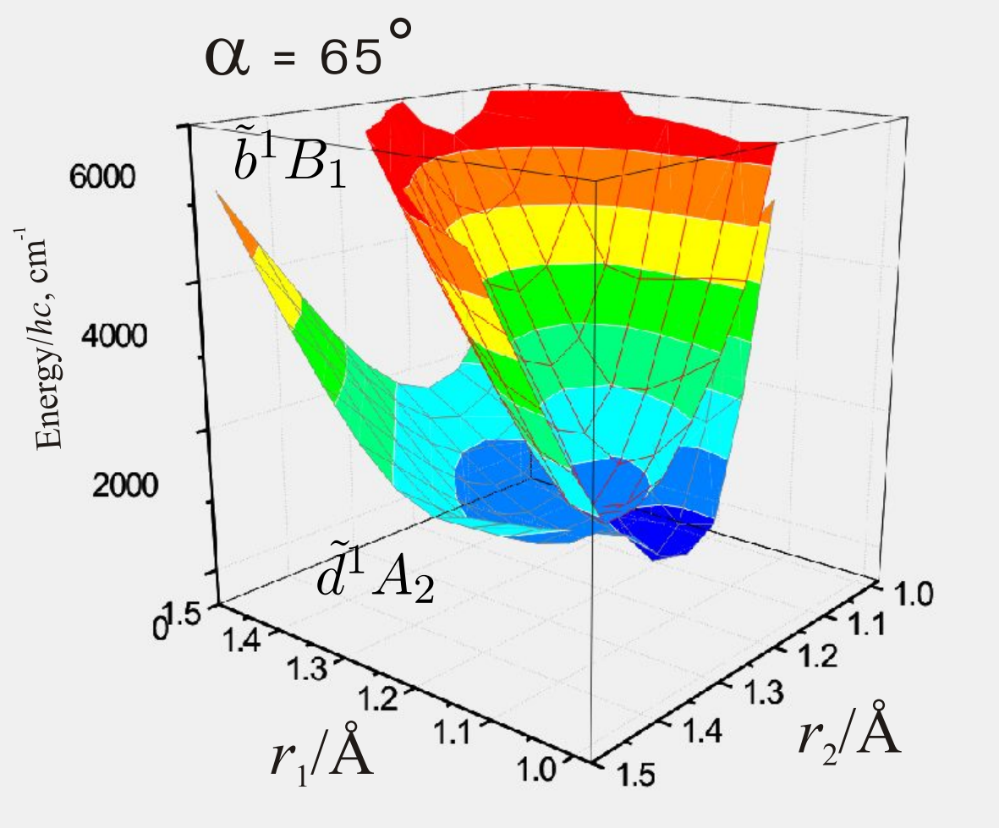
The $\tilde{d}\ ^1A_2$-state is a small bond angle state



The dissociation of singlet methylene is important in combustion and astro-chemistry. Here we investigate the predissociation of $\tilde{d}$ -state CH_2 via the reaction path $CH_2\ (\tilde{d}\ ^1A_2) \rightarrow C(^1D) + H_2(X\ ^1\Sigma_g^+)$. The singlet electronic state $\tilde{d}\ ^1A_2$ is a small-bond-angle state (α_e = 46º) with a very low dissociation energy of about 4200 cm^{-1}. There is an avoided crossing between the $\tilde{d}\ ^1A_2$ and $\tilde{b}\ ^1B_1$ states at asymmetrical geometries leading to very complex shapes of their adiabatic potential energy surfaces. We have employed a multi-reference singles-and-doubles configuration-interaction (MRCISD) method based on full-valence complete active space self-consistent field (FV-CASSCF) wavefunctions [1] as implemented in MOLPRO. The basis set consists of the cc-pV5Z(-h) and cc-pVQZ basis sets for the C and H atom, respectively, augmented with diffuse functions on the C atom. We obtained the adiabatic potential energy surface of the $\tilde{d}\ ^1A_2$ state of CH_2 as well as the adiabatic potential energy surfaces of the three interacting states.



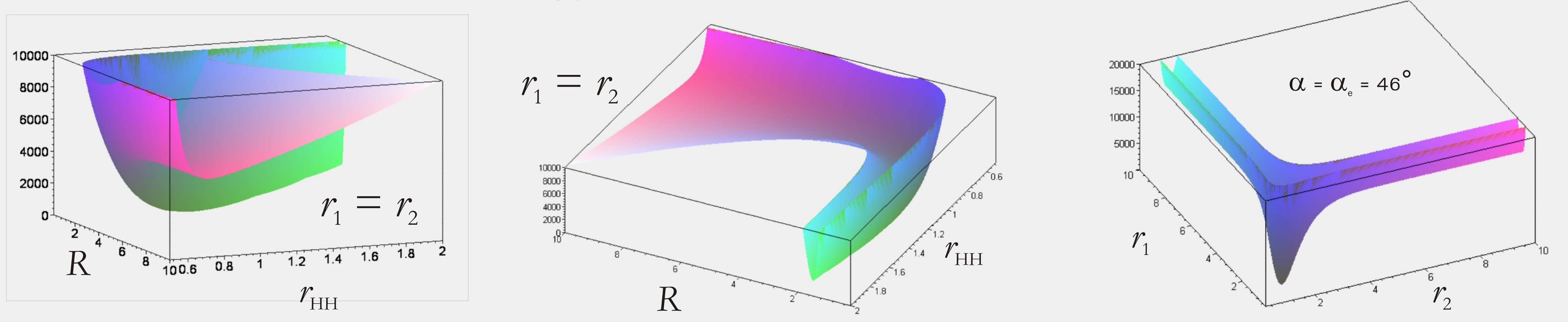
The minimum-energy bending paths for the four lowest singlet electronic states of CH_2.



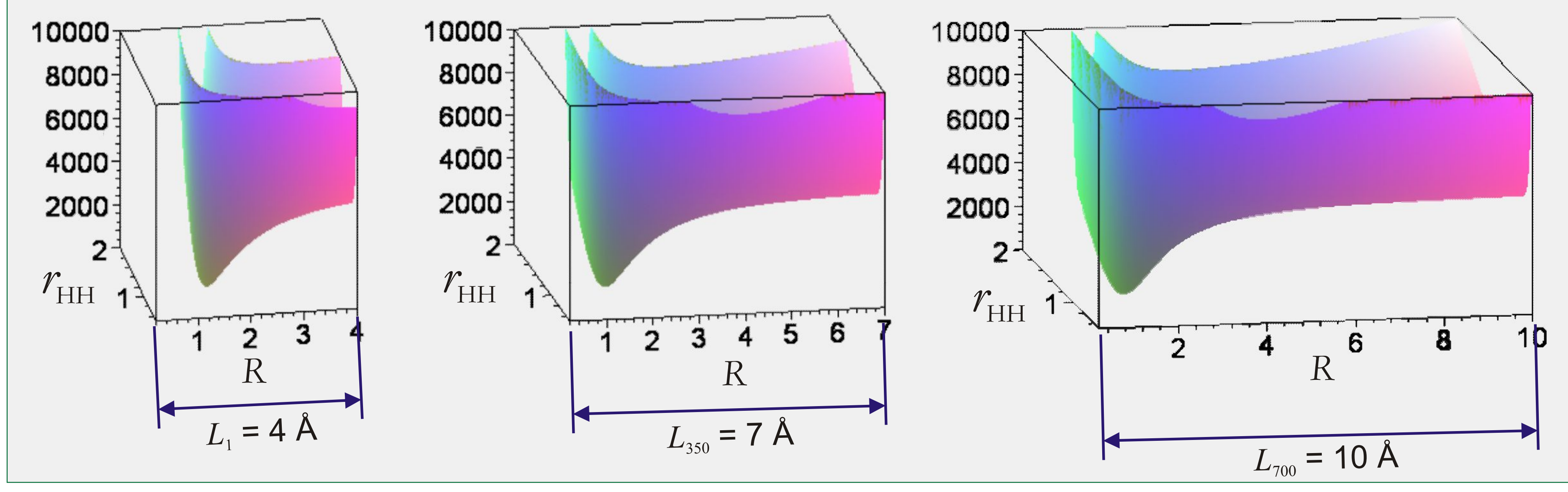
The avoided crossing between the adiabatic $\tilde{d}\ ^1A_2$ and $\tilde{b}\ ^1B_1$ PESs of CH_2 at asymmetric geometries.

[1] G. J. Vázquez, J. M. Amero, H. P. Liebermann, R. J. Buenker, and H. Lefebvre-Brion, *J. Chem. Phys.* **126**, 163302 (2007).

Diabatic potential energy surface of the $\tilde{d}\ ^1A_2$-state of CH_2



Variational solution: Stabilization method



The (quasi-)bound vibrational states were computed by means of the stabilization method by Mandelshtam *et al.* [1] in association with the variational program TROVE. The vibrational structure of the $\tilde{d}\ ^1A_2$-state up to 10000 cm^{-1} above the minimum is obtained through a full 3D calculation of the $\tilde{d}$ -state diabatic PES of CH_2.

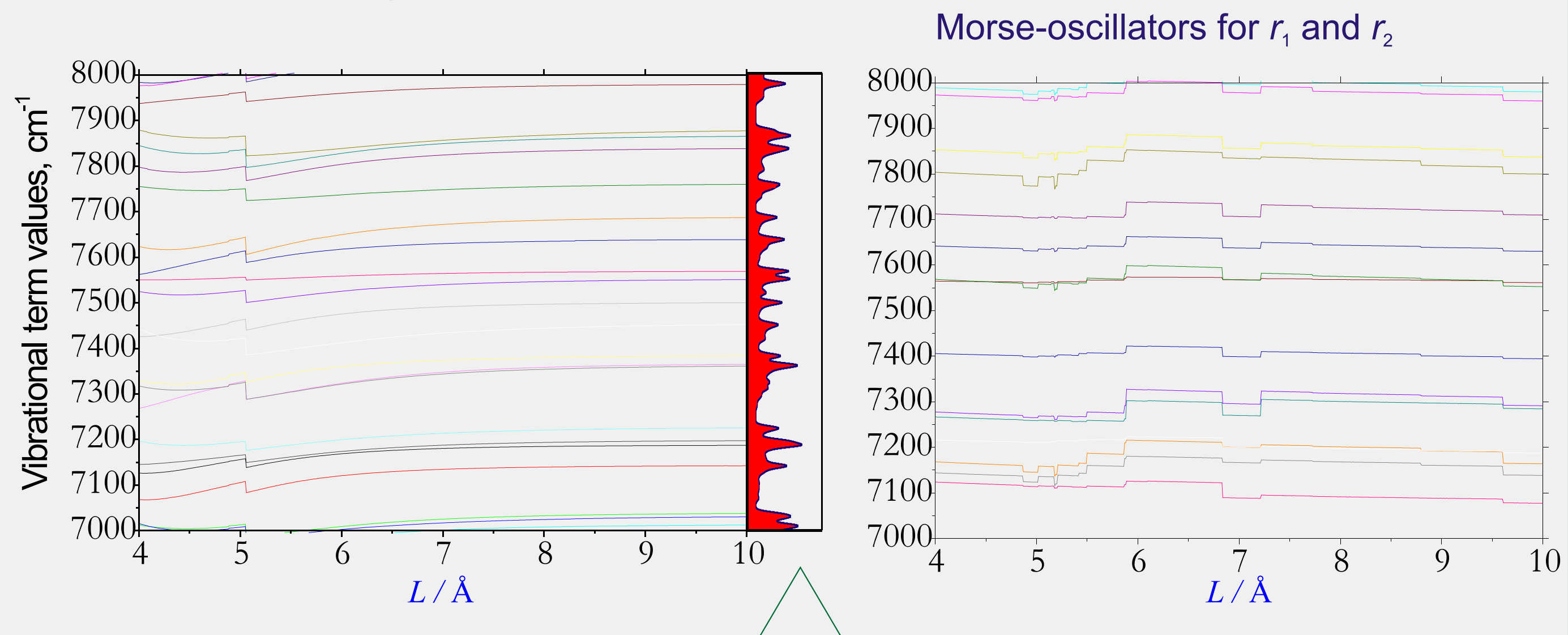
[1] V.A. Mandelshtam, T.R. Ravuri, and H.S. Taylor, *Phys. Rev. Lett.* **70**, 1932 (1993).

L_i is the length of the box, L_i = 4 to 10 Å as i =1 to 700.

Resonances in $\tilde{d}\ ^1A_2$-state CH_2

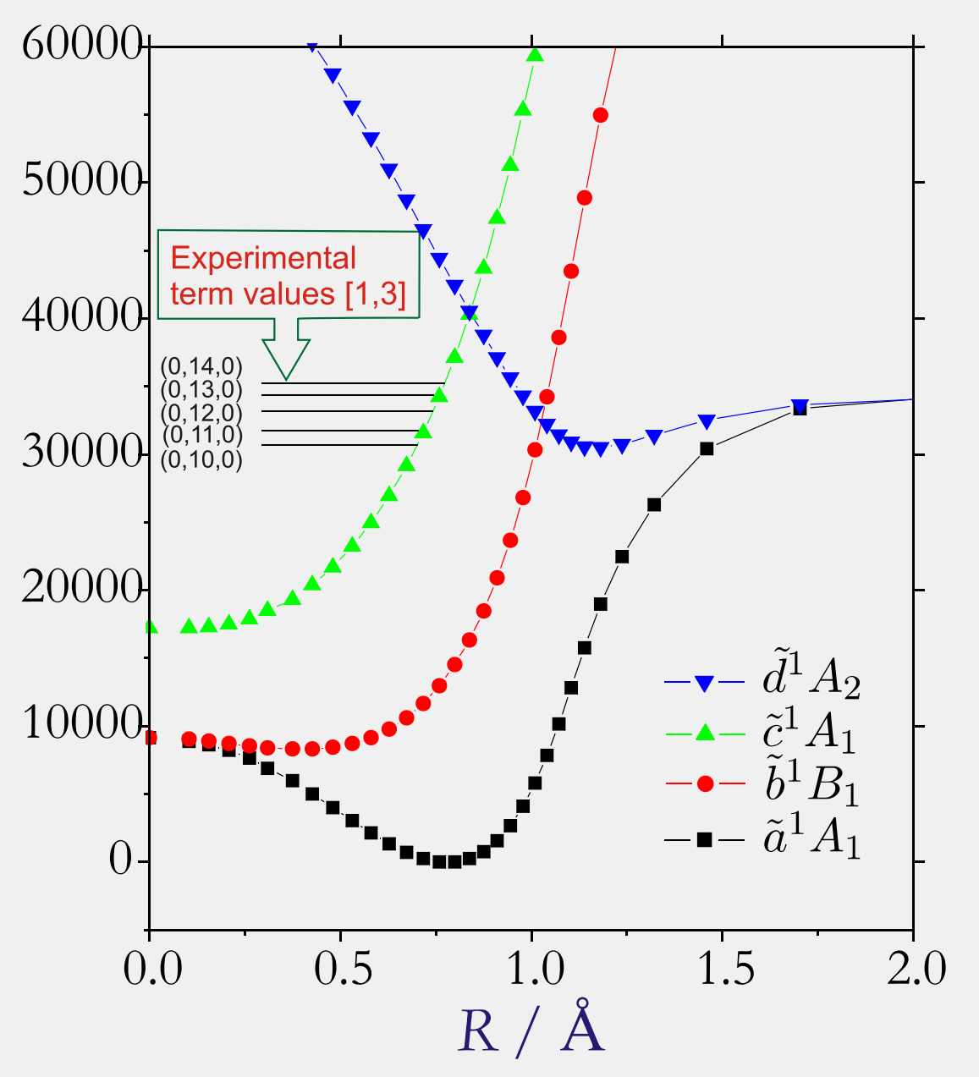
DVR representaion:

FBR representaion:
Plane waves for *R*
Morse-oscillators for r_1 and r_2



An illustration of the resonance width obtained by convoluting the distribution E_n=$E_n(L_i)$, i = 1 to 700, with a Gaussian profile (HWHM = 5 cm^{-1}), where L_1 = 4 Å and L_{700} = 10 Å.

The near ultraviolet band system of singlet methylene



The minimum-energy paths for the four lowest singlet electronic states of CH_2.

In a paper by G. Herzberg and J. W. C. Johns entitled "The Spectrum and Structure of Singlet CH_2," [1] a fragment of a weak near ultraviolet absorption band system was reported, which could not be vibrationally assigned or rotationally analyzed. The three observed bands of the system were tentatively assigned to absorption from the $\tilde{a}\ ^1A_1$ to the $\tilde{c}\ ^1A_1$ state. Herzberg and Johns also suggested that it was weak due to a combination of a small transition dipole moment and predissociation. These three bands were vibationally assigned in the theoretical study by Yurchenko *et al.* [2]. The assignements were later confirmed by Wang *et al.* [3].

[1] G. Herzberg and J. W. C. Johns, *Proc. Roy. Soc. A* **295**, 107 (1966)
[2] S.N. Yurchenko, P. Jensen; Y. Li, R. J. Buenker, and P.R. Bunker, *J. Mol. Spectrosc.* **208**, 136 (2001).
[3] Z. Wang, Y. Kim, G.E. Hall, and T.J. Sears, *J. Phys. Chem. A*, **112**, 9248 (2008).