

The ${}^2\Pi_g$ shape resonance of acetylene anion: an investigation with the RAC method^{*}

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Abstract. Recently developed method of regularized analytic continuation (RAC) is applied to determination of the ${}^2\Pi_g$ resonance of acetylene anion. The method is based on continuation of the electron affinities calculated for the anion in presence of an external perturbation field. Its independence on the correlation treatment of the many-electron system allows application of accurate coupled-clusters methods for electronic structure calculations utilized in determination of the resonance position and width.

1 Introduction

The knowledge of energies and lifetimes of electronically metastable anions plays important role in a wide variety of applications in nanotechnology [1], cancer research [2], astrochemistry [3], etc. These metastable anions are also called resonances and possess a higher energy than the ground state of the corresponding parent neutral system. Their energy is a complex quantity $E = E_R - i\Gamma/2$, with the imaginary part related to the lifetime of the resonance and the real part determining the resonance position E_R . The full treatment of these states lies within the realm of the electron-molecule scattering theory. In general, continuum states cannot be addressed using conventional electronic structure techniques. However, over the last four decades, a considerable number of methods was proposed for extraction of the resonant parameters by application of quantum chemistry methods for bound and excited states. The underlying idea of these methods is an implementation of an additional confinement to the studied negative ion system. Role of the confinement is to dampen the asymptotic part of the resonant wave function while the short-range part of the wave function remains preferably unaltered. Such procedure transfers the decaying continuum states into the bound states that are amenable to treatment by the electronic structure techniques.

Multiple variants of these methods differ in implementation of the confinement. The confinement can be enforced by an additional complex absorbing potential

(CAP) [4–6], by a rotation of the coordinate into the complex plane (complex scaling methods) [7,8], or even by a scaling of the exponents of the Gaussian basis [9] thereby scaling the space available for the resonant wave function.

The method employed in the present study was originally developed in the field of nuclear physics as the method of analytic continuation in coupling constant (ACCC) [10–12]. Its modifications for electronic structure applications have been applied with a considerable success to molecular anions of nitrogen [13], ethylene [14], carbon dioxide [15], and even to some of the DNA building blocks [16]. In contrast to the confinement methods, the ACCC method is based on a short-range modification of the Hamiltonian by a real attractive potential V

$$H(\lambda) = H + \lambda V. \quad (1)$$

Such modification pulls the resonant state from the continuum to the bound space. These bound states of the anions and the corresponding positive electron affinities $E(\lambda) = \kappa^2(\lambda)$ can be computed by commercially available quantum chemical programs. The idea of the ACCC method is based on the analytic continuation of the function $\kappa(\lambda)$ (or more precisely of its inverse function $\lambda(\kappa)$) from the bound-state domain of the positive affinities $E(\lambda)$ back to the continuum where $\kappa(\lambda)$ becomes complex and $\lambda \rightarrow 0$.

Acetylene, the smallest unsaturated hydrocarbon molecule, is isoelectronic with N_2 and may serve as one of the simplest prototypes to study π^* shape resonances often present in larger polyatomic systems. It has been, together with other hydrocarbons, employed in plasma processing in nanotechnology. Acetylene plasmas are used for preparation of diamond-like carbon thin films [17]. Acetylene represents a carbon-rich gas utilized for production of

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carbon nanotubes by dissociation of C_2H_2 and following self-assembly in plasma-enhanced chemical vapor decomposition (PECVD) process [18]. Acetylene has also been detected in natural environments where an interaction with free electrons may occur, including the interstellar medium [19] and the planetary atmospheres [20,21].

Many different aspects of the electron-acetylene collisions have been treated in previous experimental and theoretical studies. Since the focus of the present analysis is in the determination of the resonance position and width of the ${}^2\Pi_g$ resonance, only the studies dealing with this resonance will be reviewed here. Early DEA experiments [22–24] revealed a π^* -shape resonance in the energy region of 2.6–2.8 eV. This ${}^2\Pi_g$ resonance was also reported in vibrational excitation experiments [24–26] at the collision energies of 2.5–2.6 eV. The ${}^2\Pi_g$ resonance was found to dominate cross sections in absolute-value measurements of DEA of acetylene molecule. The peak in the DEA cross section was observed at 2.95 eV [27].

There have been several computational studies dealing with analysis of the ${}^2\Pi_g$ resonance. Tossell [28] utilized the continuum MS-X α approach and identified the resonance at 2.6 eV as a maximum in the calculated elastic cross section. Later Krumbach et al. [29] employed the method of configuration interaction (CI) and computed the complex resonant curve as a function of C \equiv C distance. The resonance position and width at the equilibrium geometry were reported as 2.92 eV and 1.11 eV, respectively. Single-centre expansion method with different parameter-free model potentials was utilized in two studies [30,31]. Computed fixed-nuclei elastic cross sections revealed maxima attributed to the ${}^2\Pi_g$ at 2.0 eV and 2.5 eV in the two studies. The resonance position of 2.5 eV was also confirmed by calculations [32] employing Schwinger multichannel method (SMC). Complex scaling in combination with dilated electron propagator method has been used [33] in investigation of the ${}^2\Pi_g$ resonance. While the reported resonance position of 2.58 eV agrees well with the previous data, computed width of 0.23 eV appears too low. More recently, equation-of-motion coupled-clusters (EOM-CC) method with the complex absorbing potential (CAP) was applied to identify this resonance [34]. Reported energy and width are 2.61 eV and 0.76 eV, respectively.

Three-dimensional resonant surface has been calculated in the most detailed computational study [35] of the electron-acetylene resonant collisions. The resonant surface computed by employing complex Kohn variational method was also used as input for the study of the dissociation dynamics with the local complex potential model. Authors reported resonance at 2.72 eV for the equilibrium geometry.

While most of the reported energy positions of the ${}^2\Pi_g$ resonance agree reasonably well (2.5–2.9 eV) only a few attempts to determine the lifetime of this resonance can be found in the literature. Moreover, corresponding resonance widths range from 0.23 eV [33] up to 1.11 eV [29]. Such discrepancy motivated our present study in which we apply the Regularized Analytic Continuation (RAC)

method and CCSD-T level of many-body theory to study the ${}^2\Pi_g$ shape resonance of acetylene.

2 RAC method

The method of Regularized Analytical Continuation (RAC) has been introduced and described in detail in our previous paper [36]. Here we give only brief summary and correct some typographical errors of the paper [36]. As mentioned in the introduction, the idea of the RAC approach is to replace the Hamiltonian H describing the electron molecule resonance state by a new Hamiltonian $H + \lambda V$ where $V(r)$ is an attractive perturbation able to transform the resonances state into a bound state. The coupling constant λ as function of κ with the bound state energy $-E = -\kappa^2$, has the following properties [10–12]:

- $\lambda(\kappa)$ is a real function for real κ increasing at positive κ .
- For nonzero angular momentum l the inverse function $\kappa(\lambda)$ behaves close to the threshold $\kappa = 0$ as $\kappa(\lambda) \sim \sqrt{\lambda - \lambda_0}$. As a direct consequence the function $\lambda(\kappa) \sim \lambda_0 + b\kappa^2$ at small values of κ and has therefore a local minimum at the threshold $\kappa = 0$.
- For real potentials the function $\lambda(\kappa)$ may have three types of zeros: (i) bound states lying on the physical sheet with κ positive, (ii) virtual states at negative values of κ , and (iii) pairs of resonances with $\text{Im}(k)$ negative ($k = i\kappa$) resulting in real parts of κ -plane zeros of $\lambda(\kappa)$ function being negative.

The RAC algorithm now proceeds as follows: the perturbation potential $V(r)$ is selected and bound state energy calculations are performed for a series of values λ_i for which the resonance state is transformed into a bound state. The function $\lambda(\kappa)$ represented in the form of Padé approximation is fit to the calculated data and its complex zeros describing the complex energy of the resonance state are determined. The use of Padé approximation to represent the function $\lambda(\kappa)$ allows us to extend its range for positive values of κ to the complex plane. The lowest approximation which fulfills all the requirements above can be written as

$$\lambda^{[2/1]}(\kappa) = \lambda_0 \frac{\kappa^2 + 2\alpha^2\kappa + \alpha^4 + \beta^2}{\alpha^4 + \beta^2 + 2\alpha^2\kappa}. \quad (2)$$

This function has two complex conjugate zeros

$$\kappa_{1,2} = -\alpha^2 \pm i\beta,$$

giving in k -space

$$k_{1,2} = \pm\beta - i\alpha^2,$$

and obviously describes one pair of resonances with the energy $E = \beta^2 - \alpha^4$ and width $\Gamma = 4\alpha^2|\beta|$.

Similarly one may construct higher approximations. If the pair of resonances is extended by an addition of one virtual state, we obtain [3/1] PA

$$\lambda^{[3/1]}(\kappa) = \lambda_0 \frac{(\kappa^2 + 2\alpha^2\kappa + \alpha^4 + \beta^2)(1 + \delta^2\kappa)}{\alpha^4 + \beta^2 + \kappa(2\alpha^2 + \delta^2(\alpha^4 + \beta^2))}. \quad (3)$$

In this case there is one additional parameter $-\delta$ to fit. This parameter determines the energy of the virtual state $E_v = -\delta^{-4}$. The PA [2/1] is usually a very good approximation and the resonance parameters obtained at the lower level can be used to start the fitting procedure at higher level by setting $\delta = 0$. Even higher approximations can be constructed in a similar manner. For example the PA[3/2] approximation may take the form

$$\lambda^{[3/2]}(\kappa) = \lambda_0 \frac{(\kappa^2 + 2\alpha^2\kappa + \alpha^4 + \beta^2)(1 + \delta^2\kappa)}{\alpha^4 + \beta^2 + \kappa(2\alpha^2 + \delta^2(\alpha^4 + \beta^2)) + \varepsilon^2\kappa^2}. \quad (4)$$

To incorporate two resonances in the fit we can write PA [4/2] expression as

$$\lambda^{[4/2]}(\kappa) = \lambda_0 \frac{(\kappa^2 + 2\alpha^2\kappa + \alpha^4 + \beta^2)(\kappa^2 + 2\gamma^2\kappa + \gamma^4 + \delta^2)}{(\alpha^4 + \beta^2)(\gamma^4 + \delta^2) + \mu^2\kappa + \omega^2\kappa^2} \quad (5)$$

where

$$\mu^2 = 2(\alpha^2(\gamma^4 + \delta^2) + \gamma^2(\alpha^4 + \beta^2)). \quad (6)$$

All these functions satisfy the three physical conditions described above and in all the cases the resonance energy is obtained as $E_R = \beta^2 - \alpha^4$ and the width as $\Gamma = 4\alpha^2|\beta|$. In the PA [4/2] fit the energy of the second resonance is obtained as $E_2 = \delta^2 - \gamma^4$ and the width is given by $\Gamma_2 = 4\gamma^2|\delta|$. As the order of PA increases the stability of the calculated resonance parameters decreases. Our practical experience indicates that in case of the π^* shape resonances present in anions of ethylene [14], diacetylene [36] and acetylene the [3/1] approximation represents the best compromise between accuracy and stability. Therefore, only the result for [3/1] model will be presented in this paper.

3 Affinities of acetylene

Ab initio calculations were done using the CCSD-T method [37,38] as implemented in the MOLPRO 10 package of quantum-chemistry programs [39] and Dunning's augmented correlation-consistent basis set of quadruple-zeta quality (aug-cc-pVQZ) [40]. Resulting equilibrium C \equiv C and C-H bond distances are, 1.206 Å and 1.064 Å, respectively.

Two aspects of the ${}^2\Pi_g$ resonance make this case quite challenging for the RAC method:

1. The lowest partial wave contributing to the ${}^2\Pi_g$ symmetry is the d -wave. The $l = 2$ wave modifies higher polynomial orders of the continued function when compared to previously studied cases [14,36] of the p -wave resonances and therefore it becomes more unstable to extract corresponding resonance parameters.
2. It will be shown below that the width of the resonance becomes quite large for shorter C \equiv C separations. Such conditions always possess difficulties for extraction of the resonance parameters.

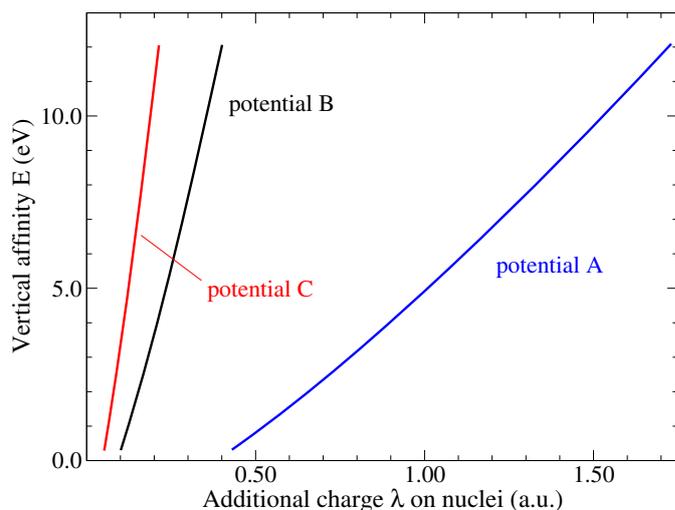


Fig. 1. Vertical electron affinity $E(\lambda)$ as a function of the charge parameter λ for three different perturbation potentials defined by equations (7)–(9) and for the equilibrium geometry of acetylene.

As a result of these complications we decided to examine, in more detail, an influence of the form of the perturbation potential V applied to the molecular Hamiltonian. We have studied three different Coulomb potentials

$$\text{A. } \lambda V(\mathbf{r}) = -\frac{\lambda}{r}, \quad (7)$$

$$\text{B. } \lambda V(\mathbf{r}) = \sum_{i=1}^2 -\frac{\lambda}{|\mathbf{r} - \mathbf{R}_i|}, \quad i = \{C_1, C_2\}, \quad (8)$$

$$\text{C. } \lambda V(\mathbf{r}) = \sum_{i=1}^4 -\frac{\lambda}{|\mathbf{r} - \mathbf{R}_i|}, \quad i = \{C_1, C_2, H_1, H_2\}, \quad (9)$$

where the case A describes a single Coulomb potential position in the centre of the molecule, the case B represents two Coulomb potentials position on the carbon atoms, and in the case C the additional Coulomb potential is placed on the all atomic centers.

Electron affinities $E(\lambda)$ in the presence of the additional fields (7)–(9) are calculated as differences between the ground state energy of the neutral molecule $E^0(\lambda)$ and the ground state energy $E^-(\lambda)$ of the negative ion

$$E(\lambda) = E^0(\lambda) - E^-(\lambda). \quad (10)$$

A typical dependence of the affinity $E(\lambda)$ on the field strength for the equilibrium geometry is shown in Figure 1 for all the three cases (7)–(9). It is obvious that fewer Coulomb centers in the perturbation potential V result in larger additional nuclear charge λ necessary to turn the resonance into a bound state.

Strictly speaking, the theory of analytic continuation outlined in Section 2 is valid only for short-range perturbation potentials V . Hence, it may seem contradictory to employ the Coulomb fields (7)–(9) in the present study. However, in our previous paper [36] we have demonstrated that Coulomb fields may be utilized in the ACCC methods

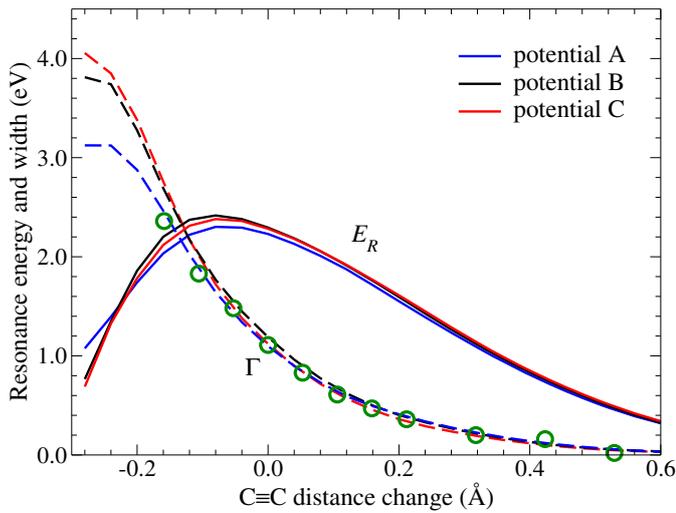


Fig. 2. Resonance positions and widths as functions of the C≡C bond length for three different perturbation potentials defined by equations (7)–(9). Full lines show the resonance positions E_R while the broken curves display the resonance widths Γ . The circles correspond to the widths calculated by Krumbach et al. [29].

if the problematic low affinity region is avoided. In this region the affinity curves switch from the valence states (shown in Fig. 1) to the Rydberg states (not shown in Fig. 1) and they become disturbing for the analytic continuation procedure. Therefore, only the affinity curves in the energy region from 0.3 eV to 12 eV (see Fig. 1) were utilized in the present study.

4 Analysis for the ${}^2\Pi_g$ resonance

Calculated resonance positions and widths for all the three perturbation potentials (7)–(9) are displayed in Figure 2 as functions of the C≡C bond length. Data in the figure exhibit very good agreement between the potential models B and C. The results for a single central potential A are slightly different and we attribute the difference to a suboptimal nature of such potential since the ${}^2\Pi_g$ resonance is formed dominantly by p -orbitals of the two carbon atoms. Moreover, with respect to the width of the resonance such deviations between different perturbation potential models are not surprising. Recommended results of the present RAC method are then results of the model B and they are summarized in Table 1. Figure 2 also reveals very good agreement of calculated resonance widths with previous calculations of Krumbach et al. [29].

In Figure 3 the complex potential energy curves of the neutral acetylene and the ${}^2\Pi_g$ resonance are displayed. The neutral ground state ${}^1\Sigma_g$ curve of reference [29] is practically identical with the CCSD-T curve of the present study and hence it is not displayed in Figure 3. In contrast to the widths displayed in Figure 2, the resonance positions of reference [29] shown in Figure 3 are systematically higher than present results. This difference may

Table 1. Resonance parameters of the ${}^2\Pi_g$ negative ion state of acetylene calculated at various C≡C bond-length changes ΔR . The calculation was carried out for the perturbation potential B and the PA [3/1] continuation model.

ΔR (Å)	Energy (eV)	Width (eV)
-0.28	0.77	3.81
-0.24	1.35	3.74
-0.20	1.86	3.28
-0.16	2.20	2.69
-0.10	2.37	2.17
-0.08	2.42	1.77
-0.04	2.38	1.45
0.00	2.29	1.19
+0.04	2.19	0.96
+0.08	2.06	0.77
+0.12	1.91	0.62
+0.16	1.76	0.50
+0.20	1.60	0.40
+0.24	1.43	0.33
+0.28	1.27	0.27
+0.32	1.11	0.21
+0.36	0.97	0.17
+0.40	0.83	0.13
+0.44	0.71	0.10
+0.48	0.60	0.08
+0.52	0.50	0.06
+0.56	0.40	0.05
+0.60	0.33	0.04

Table 2. Comparison of available results for the ${}^2\Pi_g$ resonance of acetylene at the equilibrium geometry.

Method	Energy (eV)	Width (eV)
Theory MS-X α [28]	2.6	1.0
Theory MR-CI [29]	2.92	1.11
Theory complex scaling [33]	2.58	0.23
Theory CAP EOM-CC [34]	2.61	0.76
Theory CAP EOM-CC [5]	2.450	0.831
Theory scat. SCE [30]	2.0	–
Theory scat. SCE [31]	2.5	–
Theory scat. SMC [32]	2.5	–
Theory scat. Kohn [35]	2.72	–
Theory present results	2.29	1.19
Experiment vib. excit. [25]	2.6	>1.0
Experiment vib. excit. [26]	2.5	–
Experiment transmission [24]	2.6	–
Experiment DEA [27]	2.95	–

be caused by the different correlation treatment of previously used MRD-CI method [29] and present CCSD-T approach. In our previous study [36] we already observed that better correlation model generally results in lower resonance energies while the widths change very little. This observation is also in accord with different correlation models employed in reference [29] where authors report very weak dependence of the resonant widths on the correlation treatment.

In Table 2 we attempt to summarize available results for the parameters of the ${}^2\Pi_g$ resonance. It is evident that the present study predicts the resonance position

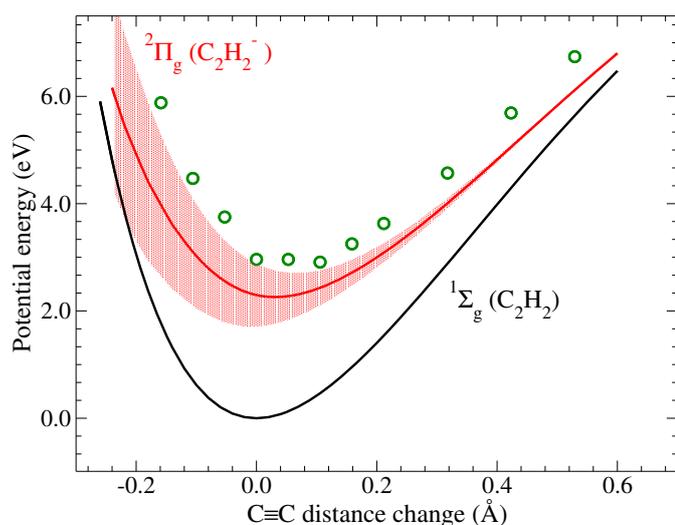


Fig. 3. Potential energy curve for the ground state $^1\Sigma_g$ of the neutral acetylene molecule (black curve) as a function of C \equiv C bond length. Real part of the potential energy curve for the temporary negative ion state $^2\Pi_g$ is displayed by the thick red curve. Vertical height of the filled area shows the width Γ corresponding to the anion resonant state. Circles are the energies of the resonant state calculated by Krumbach et al. [29].

lower than most of the previous calculations. Remarkably, Krumbach et al. [29] applied the resonant boomerang model for calculations of vibrationally inelastic cross sections. They have shown that the peak of the vibrationally inelastic cross section for the excitation $0 \rightarrow 1$ is positioned about 0.2 eV above their calculated equilibrium resonant position. Hence, we believe the vibrational excitation experiments may suggest that the vertical resonant position should be somewhere around 2.3–2.4 eV in fairly good agreement with present results. Moreover, peak of the DEA cross section computed at 2.998 eV in reference [35] is localized again about 0.2 eV above the computed vertical resonance position of 2.72 eV. Such a coincidence may be fortuitous or it may point to a physical mechanism that is common for the two processes such as the entry amplitude defined by the energy-dependent Franck-Condon factor.

5 Conclusions

The RAC method is a variant of the known method of analytical continuation in the coupling constant but, owing to the physical constraints imposed on the continued function, it is considerably more stable and robust. In the present study the RAC approach was employed to determine the position and width of the $^2\Pi_g$ resonance of acetylene anion. Because of the challenging nature of the resonance (mainly due to the large width) we examined the impact of different choices for the perturbation potential. We found that the resulting complex resonant energies depend only weakly on the perturbation potential choice thus reinforcing confidence in the capability of the RAC procedure.

Since the RAC method is based on the analytical continuation of affinities for a bound-state system, it is independent of the correlation model employed for the many-electron Hamiltonian. Such flexibility facilitated application of coupled-clusters level of theory (CCSD-T) to determine the $^2\Pi_g$ resonance. Calculated potential energy curve for the width of the resonance is in excellent agreement with previous calculations of Krumbach et al. [29]. However, present results predict the equilibrium vertical position at 2.29 eV, which is lower (by 0.2–0.6 eV) than most of the previous theoretical results (see Tab. 2). We believe that present lower values may, in fact, be in a good agreement with the experimental data for the vibrational excitation that see the center of the excitation peak at 2.5–2.6 eV. This conclusion is based on the previous calculations [29] demonstrating that the computed peaks for the vibrational excitation of acetylene should be about 0.2 eV higher than vertical equilibrium resonant position.

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