This is the accepted manuscript made available via CHORUS. The article has been published as:

Simplified model to treat the electron attachment of complex molecules: Application to $\text{H}_2\text{CN}$ and the quest for the $\text{CN}^\sim$ formation mechanism
C. H. Yuen, N. Douguet, S. Fonseca dos Santos, A. E. Orel, and V. Kokouline
Phys. Rev. A 99, 032701 — Published 1 March 2019
DOI: 10.1103/PhysRevA.99.032701
Simplified model to treat the electron attachment of complex molecules: Application to H$_2$CN and the quest for CN$^-$ formation mechanism

C. H. Yuen,¹ N. Douguet,¹ S. Fonseca dos Santos,² A. E. Orel,³ and V. Kokouline¹

¹Department of Physics, University of Central Florida, Orlando, Florida 32816, USA
²Department of Physics, Rollins College, Winter Park, Florida, 32789, USA
³Department of Chemical Engineering and Materials Science, University of California, Davis, California 95616, USA

We present a simplified approach to the dissociative electron attachment of polyatomic molecules. A reduced nuclear coordinate driving the dissociative process immediately following the resonance capture is introduced and allows an estimation of the cross section. The model is applied to the H$_2$CN molecule, which is considered as a precursor in the formation of the CN$^-$ anion observed in the IRC +10216 carbon star. The computed rate coefficient suggests that the dissociative electron attachment of H$_2$CN may not be an efficient reaction to form CN$^-$ in the circumstellar envelope of IRC +10216.

I. INTRODUCTION

The theoretical study of dissociative electron attachment (DEA) in large molecules is notoriously difficult due to the multi-dimensional nature of the problem. Because treatments of DEA in full dimensionality for complex systems is beyond current computational capabilities, a great deal of work has been conducted to unravel the underlying DEA mechanisms, e.g., by singling out one specific bond breaking, sorting out main dissociative pathways, or considering a subspace of coordinates [1–11]. Review of recent progress for DEA can be found in Ref. [12]. Only for a few triatomic systems, namely HCN [13, 14], ClCN and BrCN [15], could a complete treatment be performed, while DEA for such “basic” triatomic molecules as H$_2$O [16–21] and CO$_2$ [22, 23], where multiple electronic states of the target molecule and nonadiabatic couplings should be taken into account, are still actively studied presenting a great deal of difficulty.

The formidable task of describing DEA in polyatomic molecules has often hindered the computation of DEA rate coefficients crucial for astrophysical models [24–26]. In fact, even an estimate of such rates is usually sufficient to understand the role played by specific reactions in the formation and destruction of molecules in the interstellar medium (ISM). Here, we propose a simplification of the computation of DEA cross sections by generalizing the model of O’Malley and Bardsley [27] to systems with many coordinates in order to obtain an estimation of the resonant capture cross section. The model is applied on the DEA of H$_2$CN which is closely related to the unsolved problem of CN$^-$ formation in the ISM.

The density distribution of CN$^-$ molecular anions observed in IRC +10216 [29] still puzzles physicists to date. Indeed, the carbon chain C$_n^-$ and C$_n$H$^-$ are considered to play a predominant role in the formation of CN$^-$ upon collision with N atoms [30, 31], however, chemical models predict CN$^-$ density produced by these reactions to peak in the outer region of the circumstellar envelope of IRC +10216, while the fitted density distribution peaks in the inner region [29].

This discrepancy suggests that reactions responsible for the CN$^-$ production in the inner region of the envelope have been overlooked. Other than the reaction with C$_n^-$ and C$_n$H$^-$, collision of HCN with H$^-$ and radiative electron attachment (REA) of CN also produce CN$^-$ in the inner region. In the chemical model used by Agundez et al. [29], the temperature-independent Langevin rate of the former reaction was used and was shown to contribute less than 0.2% of the total amount of CN$^-$. The latter reaction has recently been studied by Satta et al. [32] using variational transition state theory. They found a strong temperature dependence on the rate coefficient and suggest that an extensive chemical model may produce CN$^-$ more efficiently in the hotter inner region. In addition, a high density of H$^-$ in the inner region could enhance this barrier-less reaction. On the other hand, an ab inito calculation by Douguet et al. [33] found that the rate coefficient for formation of CN via REA is too slow to produce CN$^-$ in the inner region.

In this article, we propose that a significant part of CN$^-$ observed in the inner region originates from the DEA of the open-shell molecule H$_2$CN, i.e.

$$\text{H}_2\text{CN}(X^2\text{D}_2) + e^- \rightarrow (\text{H}_2\text{CN})^{-}\Theta^+(1\text{A}_1)$$

$$\rightarrow \text{CN}^-(X^1\Sigma^+) + \text{H}_2(X^1\Sigma^+_g)$$

$$\rightarrow \text{HCN}(X^1\Sigma^+) + \text{H}^-(1\text{S}),$$

(1)

where the first and second dissociation channels are both exothermic by 1.92 and 0.6 eV respectively. The H$_2$CN molecule was first detected in the cold dark molecular cloud TMC-1 in 1994 [34]. Soon after, Millar and Herbst proposed the existence of H$_2$CN in the circumstellar envelope of the carbon-rich star IRC +10216 by including the neutral-neutral reaction N + CH$_3$ → H$_2$CN +H in their chemical model [35, 36].

Since the gas density in the ISM is low, open-shell species have longer life time than in the laboratory. Therefore, if the rate coefficient for reaction (1) is fast enough, it could resolve the discrepancy of CN$^-$ density between the chemical model and observation.
II. TARGET AND RESONANCES

We employ the MOLPRO suite of programs [37] to determine the electronic structure and vibrational frequencies of H$_2$CN. We first perform the calculation using multi-reference configuration interaction (MRCI) [38, 39] with Hartree-Fock (HF) orbitals. The basis set for all atoms are chosen to be cc-pVQZ [40]. In the MRCI calculation, the 1s and 2s carbon and nitrogen core orbitals are frozen and we include 8 active orbitals in the complete active space (CAS). At the equilibrium geometry, the bond lengths CH, NH, and the HCH angle, are found to be 1.088 Å, 1.246 Å, and 121.1°, respectively. H$_2$CN at the equilibrium possesses $C_{2v}$ point group symmetry, with ground state electronic configuration

$$X^2B_2 : 1a_1^2a_2a_3^2a_4^2a_1b_2^2a_1^2b_1^22b_2.$$  

We then computed the harmonic frequencies and compared with theoretical [41, 44–48] and experimental studies available in the literature [42, 43]. In Tab. I we compare our results with Ref. [41] and the experimental studies [42, 43]. We observe a good agreement between our results and the calculations [42] and only small discrepancies with the experimental results. We use normal coordinates in the present study.

![Graph showing the variation of resonance energies](image)

FIG. 1. (Color online) The scattering eigenphase sum for total symmetry $^1A_1$, $^3A_2$, and $^1A_2$. The solid and dashed lines are the results obtained from CASCI model and static exchange model respectively.

To compute the resonance position $\Delta(\vec{q})$ and width $\Gamma(\vec{q})$ at a given molecular geometry $\vec{q}$, we use the UK R-matrix code [49, 50] in QUANTEMOL-N suite [51] for electron-molecule scattering to obtain the R-matrix. To be consistent with the MOLPRO calculation, we use a complete active space configuration interaction (CASSCI) model to compute the electronic structure of the target using the same basis set, molecular orbitals, number of frozen orbitals, and complete active space. Eigenphase sums are fitted using the Breit-Wigner, providing resonance energies and widths [52]. At electron energy below 5 eV, and at H$_2$CN equilibrium geometry, we found three shape resonances: $^1A_1 (\Delta = 0.277$ eV, $\Gamma = 8.24$ meV), $^3A_2 (\Delta = 2.56$ eV, $\Gamma = 1.2$ eV), and $^1A_2 (\Delta = 3.15$ eV, $\Gamma = 1.49$ eV).

Figure 1 displays the eigenphases sum obtained from static exchange model and CASCI model for total symmetry $^1A_1$, $^3A_2$, and $^1A_2$. Since H$_2$CN has large polarizability $\alpha$, the static exchange model neglects a substantial gain of kinetic energy of electron from the $-\alpha \cdot \hat{r} / 2 r^5$ potential, with $\alpha \approx 1.33 a_0^3 \hat{r}$. Therefore, position of resonances from the static exchange model are at higher energies than the CASCI model. Nevertheless, the fact that those three resonances are seen in the static exchange model implies that all the resonances are shape resonances.

A similar R-matrix calculation was reported by Wang et al. [53] who also found the $^3A_2$ and $^1A_2$ shape resonance at similar positions but with widths two orders smaller than our results. Moreover, they did not find the $^1A_1$ shape resonance at low energy most likely because they use a relatively small basis set. We have ascertained that the position and width of the lowest resonance remain relatively stable with respect to the variation of the size of the R-matrix box, the size of the complete active space, and the basis set.

Analyzing the symmetry, one can deduce the possible dissociation products from certain resonance states. For the two dissociation channels in (1), the total spin of the system is zero, so that resonance in triplet state cannot lead to dissociation. To dissociate into CN$^−(X^1\Sigma^+) +$ H$_2(X^1\Sigma^+)$ or HCN($X^1\Sigma^+) +$ H$^−(^1S)$, the system must be symmetric with respect to reflection on the plane spanned by CN$^− +$ H$_2$ or HCN + H$^−$. However, upon symmetry breaking, $^1A_2$ becomes $^1A''$ irreducible representation in $C_s$ group, such that it is anti-symmetric with

![Graph showing the variation of resonance energies](image)

FIG. 2. (Color online) The variation of resonance energies $\Delta(\vec{q})$ (in eV) over $q_1$ (black circles), $q_2$ (red squares), $q_3$ (green diamonds), $q_4$ (blue triangles up), $q_5$ (brown triangles down) and $q_6$ (violet crosses) for H$_2$CN.
TABLE I. Calculated and experimental harmonic frequencies $\omega$ (in cm$^{-1}$) for each $q$. Our result is compared with the result from CISD+Q/cc-pVTZ method [41]. Experimental frequencies are obtained from [42], except for $\omega_5$, which is from [43].

\begin{tabular}{|c|c|c|c|c|c|c|}
\hline
$\omega_1$ & $\omega_2$ & $\omega_3$ & $\omega_4$ & $\omega_5$ & $\omega_6$ \\
\hline
CH$_2$ rock ($B_2$) & out of plane ($B_1$) & CH$_2$ scissor ($A_1$) & CN stretch ($A_1$) & CH$_2$ sym stretch ($A_1$) & CH$_2$ asym stretch ($B_2$) \\
This study & 967.2 & 995.3 & 1420.6 & 1706.6 & 3080.0 & 3140.7 \\
Ref. [41] & 957.1 & 994.4 & 1401.6 & 1692.4 & 3031.9 & 3102.7 \\
Experiment & 912.8 & 954.1 & 1336.6 & 1725.4 & 2820 & 3103.2 \\
\hline
\end{tabular}

III. THEORY OF RESONANT CAPTURE

In order to find the steepest descent or capture coordinate, we seek an orthogonal matrix which transforms ($q_3, q_5$) to ($s_1, s_2$),

$$
\begin{pmatrix}
\alpha & \beta \\
-\beta & \alpha
\end{pmatrix}
\begin{pmatrix}
q_3 \\
q_5
\end{pmatrix} =
\begin{pmatrix}
s_1 \\
s_2
\end{pmatrix}.
$$

Choosing $s_1$ as the capture coordinate leads to

$$
\frac{\partial \Delta}{\partial s_1} = \alpha \frac{\partial \Delta}{\partial q_3} + \beta \frac{\partial \Delta}{\partial q_5},
$$

where the constants $\alpha$ and $\beta$ are

$$
\alpha = \frac{|\partial \Delta / \partial q_3|}{\sqrt{(\partial \Delta / \partial q_3)^2 + (\partial \Delta / \partial q_5)^2}} ; \quad \beta = \sqrt{1 - \alpha^2}.
$$

Since the width of the resonance is narrow, we neglect the explicit energy dependence of the width, i.e., we only consider the on-shell width. In the so-called local complex potential approach [27, 54, 55], the metastable state $\xi_d$ becomes solution of the following equation

$$
\left[ \hat{T} + U_d(q) - \frac{i\Gamma(q)}{2} - E \right] \xi_d(q) = V_d(q) \zeta(q),
$$

$$
V_d(q) = \frac{\sqrt{\Gamma(q)}}{2\pi},
$$

where $\hat{T}$ is the nuclei kinetic energy operator, $U_d$ is the resonance energy plus the neutral potential energy, and $\zeta$ is the ground vibrational wave function of the target.

In our model, only the coordinates $q_3$ and $q_5$ participate in the capture process. Thus, in the spirit of the sudden approximation, we write the nuclei wave function $\xi_d$ as

$$
\xi_d(q) \approx \xi_c(q_3, q_5) \chi(q^d),
$$

where $\chi(q^d)$ collects all the spectator coordinates and $\chi(q^d)$ is the product of vibrational wave functions in the spectator coordinates. Similarly, we express the vibrational wave function of the target as

$$
\zeta(q) \approx \zeta_c(q_3, q_5) \chi(q^c).
$$
We further express
\[ \dot{T} = -\frac{\hbar \omega_3}{2} \frac{\partial^2}{\partial \xi^2} - \frac{\hbar \omega_5}{2} \frac{\partial^2}{\partial \eta^2} + \dot{T}_{\text{spec}}, \]  
(8)
\[ \dot{T}_{\text{spec}} = -\sum_i \frac{\hbar \omega_i}{2} \frac{\partial^2}{\partial q_i^2}, \]  
(9)
and
\[ U_d(\vec{q}) = U_n(q_3) + U_n(q_5) + \Delta(\vec{q}) + U_{\text{spec}}(\vec{q}), \]  
(10)
\[ U_{\text{spec}}(\vec{q}) = \sum \nu U_n(q_{\nu}), \]  
(11)
where \( U_n \) are the neutral potential energies and the summation on \( \nu \) runs over all spectator coordinates. Note that \( \chi(\vec{q}') \) is the eigenfunction of \( \dot{T}_{\text{spec}} + U_{\text{spec}} \) with eigenvalue equals to the sum of zero-point energies of all spectator coordinates.

Next, multiplying \( \chi(\vec{q}') \) on the left in Eq. (5) and integrating over \( \vec{q}' \), we obtain the two dimensional equation in dimensionless coordinates,
\[ \left[ -\frac{\hbar \omega_3}{2} \frac{\partial^2}{\partial \xi^2} - \frac{\hbar \omega_5}{2} \frac{\partial^2}{\partial \eta^2} + U_n(q_3) + U_n(q_5) + \Delta(q_3, q_5, \vec{0}) - \frac{i\Gamma(q_3, q_5, \vec{0})}{2} - E \right] \xi_d(q_3, q_5)
\]  
\[ = V_d(q_3, q_5, \vec{0}) \zeta_d(q_3, q_5), \]  
(12)
where we approximate the integrals of resonance energy and width with \( \chi^2 \) over spectator coordinates at the resonance energy and width at \( \vec{q}' = 0 \).

Transforming \((q_3, q_5)\) to \((s_1, s_2)\) we then obtain
\[ \left[ \dot{T}_s + U_d(s_1, s_2) - \frac{i\Gamma(s_1, s_2)}{2} - E \right] \xi_d(s_1, s_2)
\]  
\[ = V_d(s_1, s_2) \zeta_d(s_1, s_2), \]  
(13)
where the operators \( \dot{T}_s \) is given by
\[ \dot{T}_s = -\frac{\hbar \omega_1}{2} \frac{\partial^2}{\partial s_1^2} - \frac{\hbar \omega_2}{2} \frac{\partial^2}{\partial s_2^2} - \hbar \alpha \beta (\omega_5 - \omega_3) \frac{\partial^2}{\partial s_1 \partial s_2}, \]  
(14)
while the potential \( U_d \) takes the form
\[ U_d(s_1, s_2) = \frac{1}{2} \tilde{\omega}_1 s_1^2 + \frac{1}{2} \tilde{\omega}_2 s_2^2 + \Delta(s_1, s_2)
\]  
\[ + \hbar \alpha \beta (\omega_5 - \omega_3) s_1 s_2, \]  
(15)
with
\[ \tilde{\omega}_1 = \alpha^2 \omega_3 + \beta^2 \omega_5, \]
\[ \tilde{\omega}_2 = \beta^2 \omega_3 + \alpha^2 \omega_5, \]
\[ \zeta_c(s_1, s_2) = \zeta_c(q_3, q_5) = \frac{1}{\sqrt{\pi}} \exp[-(s_1^2 + s_2^2)/2]. \]

Denoting \( \xi(s_1) \equiv \pi^{-1/4} \exp(-s_1^2/2) \), we apply the sudden approximation again and have \( \xi_d(s_1, s_2) \approx \xi_1(s_1) \xi_2(s_2) \). Multiplying \( \zeta_2(s_2) \) on both sides and integrating, we finally arrive at
\[ \left[ -\frac{\hbar \tilde{\omega}_1}{2} ds_1^2 + U_d(s_1, 0) - \frac{i\Gamma(s_1, 0)}{2} - E \right] \xi_1(s_1)
\]  
\[ = V_d(s_1, 0) \xi_1(s_1), \]  
(16)
\[ U_d(s_1, 0) = \frac{1}{2} \tilde{\omega}_1 s_1^2 + \Delta(s_1, 0), \]  
(17)
where the cross terms of \( s_1 \) and \( s_2 \) vanish as \( \zeta_2(s_2) \) is an even function. The energy \( E \) is the sum of zero-point energy of \( s_1 \) and energy of the scattering electron \( \varepsilon \).

Finally, following the WKB approach by O’Malley [27] or Bardsley [28] and assuming the survival probability of the complex is unity, the capture cross section is given by
\[ \sigma_{\text{cap}}(\varepsilon) = g \frac{2\pi^2}{k^2} \frac{\Gamma(s_c)}{|U_d'(s_E)|^2}, \]  
(18)
where \( g \) is the ratio of statistical weight of product to reactant, and the classical turning point \( s_E \) and Frank-Condon point \( s_c \) are obtained by solving \( U_d(s_E) = E \) and \( \Delta(s_c) = \varepsilon \), respectively. The statistical weight for the product \( \text{H}_2 + \text{CN}^- \) (\( X^1\Sigma_g^- \otimes X^1\Sigma^+ \)) is 1, while for the reactant \( \text{H}_2\text{CN} (2 \text{B}_2) \) is 2, such that \( g = 1/2 \).

IV. RESULTS AND DISCUSSION

Figure 3 displays the resonance energy, anionic and neutral potential energies as functions of the capture coordinate \( s_1 \). The red line shows the first order approximation of \( \Delta(s_1) \),
\[ \Delta(s_1) \approx \Delta(0) + \frac{d\Delta}{ds_1}(0)s_1, \]
FIG. 3. The anionic potential energy \( U_d \) (blue dashed line), neutral potential energy \( U_n \) (black line) and resonance energy \( \Delta \) (circles) and its linear approximation (red straight line) along \( s_1 \) for \( \text{H}_2\text{CN} \) at \( s_2 = 0 \). The black dashed line is the zero-point energy of the nuclei for coordinate \( s_1 \).
which is seen to agree well with the data points for $-1 < s_1 < 1$. The blue dashed line is obtained by adding the resonance energy to the neutral potential energy. However, we note that as the electronic wave function of the neutral target may not be well-represented with the limiting complete active space, the minimum of the anionic potential energy is above the neutral, in contradiction to the photodetachment experiment [43]. In order to obtain the correct electron affinity, we use the ab initio data obtained from RCCSD(T)/aug-cc-pVQZ [45] and shift the anionic potential energy down by 0.65 eV, which is shown as blue solid line. Since there is a local minimum for the anion potential, it suggests that there is at least one barrier in the dissociation pathway to CN$^-$ + H$_2$ or HCN + H$^-$. In our simplified model, we assume that the barrier height is smaller than 0.6 eV, such that there is no reflection of the outgoing flux from the barrier and the complex will eventually dissociate without autodetachment. At zero electron energy, the classical turning point $s_E$ is around -1.4, such that the capture process occurs in a well-defined region of normal coordinates, thereby justifying our approach.

Figure 4 shows the effective width against effective resonance energy $\Delta(s_\varepsilon)$, which is equal to electron energy $\varepsilon$ in this approach as to enforce the threshold behavior [55]. The electronic structure calculations give the value 0.957 $e a_0$ for the permanent dipole moment of H$_2$CN as at $s_1 = 1.25$. This value of $s_1$ is only 0.04 $a_0$ away from the crossing point of the original anionic and neutral potential energy curves (blue dashed and black curves in Fig. 3). Since $s$-wave scattering is forbidden by symmetry, an estimation of the off-diagonal element of dipole moment between $p, d$ and $f$ partial waves reveals that the lowest three effective orbital angular momenta $\ell$ becomes 0.939, 2.01 and 3.02, respectively [56]. To include the contribution from the lowest three partial waves, the effective width is fitted as

$$\Gamma(\varepsilon) = \sum_i a_i \varepsilon^{\ell_i + 1/2}, \quad (19)$$

where $a_1 = 0.0356, a_2 = 0.0258$ and $a_3 = 0.137$. Near threshold, we then have $\Gamma(\varepsilon) \propto \varepsilon^{2.439}$. To calculate the cross section with the shifted anionic potential curve, we use the same effective width as a function of electron energy. This is justified because the electron energy is set to equal the resonance energy in our approach. As we offset the resonance energy, the effective width will be zero at the new crossing point between the shifted potential and the neutral potential. Therefore, the effective width is also shifted in terms of coordinate implicitly. In addition, threshold behavior of the width only changes slightly as we shifted the anionic potential curve. Indeed, at $s_1 = -1.5$, the permanent dipole moment of H$_2$CN only differs by about 6% from the value at $s_1 = 1.25$. By fitting the effective width with new $\ell$, we found that the capture cross section also changes by about 6%.

Figure 5 displays the capture cross section versus electron energy. Near threshold, the cross section grows with electron energy as $\varepsilon^{0.439}$. The peak of the cross section is located near 0.1 eV. Around 1 meV, the cross section is about $3.68 \times 10^{-20}$ cm$^2$, which is about two orders magnitude larger than the cross section for the radiative electron attachment to CN [33].

Using the standard formula

$$k(T) = \frac{8\pi}{(2\pi k_b T)^{3/2}} \int \varepsilon \sigma(\varepsilon) e^{-\varepsilon/k_b T} d\varepsilon,$$

where $k_b$ is the Boltzmann constant, we obtain the thermally averaged capture rate coefficient. The rate coefficient is fitted within 1% relative error using the form $k(T) = a_1(T/300)^{a_2} e^{a_3 T^{a_4}}$ with $a_1 = 2.43 \times 10^{-12}, a_2 = 0.97025, a_3 = -9.20 \times 10^{-3}$ and $a_4 = 0.677$. The rate coefficient at 30 K is found to be about $2.36 \times 10^{-13}$ cm$^3$/s, which is two orders larger than the REA of CN [33].
one order larger than the reaction of HCN + H– [32]. Assuming the rate coefficient of electron capture is equal to the rate coefficient of forming CN– by DEA and the ratio of H2CN density to CN to be 1000 [36], we have

\[
\frac{[e^{-}]|CN|k_{REA}}{[e^{-}]|H_2CN|k_{DEA}} \approx 10
\]

at 30 K, such that DEA of H2CN is at least 10 times less efficient in producing CN– than REA of CN. Hence, our result suggests that DEA of H2CN may not play a major role in the formation of CN– in the circumstellar envelope of IRC +10216. Other possible radicals that could produce CN– by DEA in IRC +10216 are MgNC [57, 58], MgCN [59], SiCN [60], SiNC [61], FeCN [62] and CCN [63], where all species have been detected in IRC +10216. It is possible that CN– anions are produced by DEA of several of the above molecules efficiently in the inner region of the circumstellar envelope.

V. UNCERTAINTY ESTIMATION

As in many similar theoretical studies, there are two types of uncertainties [64]. One is related to the uncertainties of the theoretical model and the second type is related to the choice of parameters of the model (such as a limited basis set and uncertainties in ab initio or fitted data employed in the given model). In the present case, the main source of the first type of uncertainties is probably due to the reduced dimensionality approximation used in the present treatment and the neglect of the autodetachment process once the electron is captured into the dissociative coordinate. The uncertainties of the model can only be estimated if there is another more accurate model. For example, a fully-dimensional time-dependent propagation model similar to the used in Ref.[3] could be used to benchmark the present results.

The evaluation of the second type of uncertainties is possible. The uncertainty of the cross section can be estimated by performing R-matrix calculations with various complete active space, R-matrix radii and basis sets. At equilibrium geometry, the position and width of the resonance differ, respectively, by at most 20% and 25% by varying the complete active space from 8 to 11 molecular orbitals and R-matrix radii from 10 to 14 bohrs with basis sets cc-pVTZ or cc-pVQZ. As a result, the capture cross section, which is proportional to the effective width, has associated uncertainty of about 25%.

The second source of uncertainty arises from the off set of the anionic potential energy. The relative error between the ab initio data used [45] and the experiment is about 2%. We found that changing the shifting by 2% leads to the change of cross section by about 7%. In the most unfortunate case, if we decrease the shift by 20%, the capture cross section increases by about a factor of 2. Therefore, our approach for H2CN gives a reasonable orders of magnitude of the capture cross section.

VI. CONCLUDING REMARKS

The new approach presented in this article is based on the fact that, in general, the resonance energy varies substantially only over a subset of normal coordinates. As the resonance energy is nearly constant over H2CN normal coordinates of the Cs symmetry, we expect our approach to work also for other polyatomic molecules. For instance, the DEA of acetylene starts with bending the molecule [3], such that the corresponding normal coordinate is responsible for the capture step in the process.

The present approach has several limitations: The survival probability is assumed to be unity. Therefore, our approach gives an upper bound of the DEA cross section within the Frank-Condon and WKB approximations. Also, the width is assumed to be on-shell, so that our approach would work only for systems with narrow resonances [55]. But if the width is narrow enough, the survival factor is closed to unity, so that the two limitations are in fact equivalent. Finally, our approach cannot predict branching ratios of the dissociation products. By constructing a multidimensional anionic potential energy surface, it is possible to determine branching ratios by propagating wave packets. But this method is computationally expensive and will be reserved for future study.

To date, it is still a very challenging task to include the non-local operator to polyatomic molecule with several dissociation coordinates. Even for the local complex potential model, it is computationally demanding to compute resonance positions and widths at different geometries and perform time-dependent calculations. Besides, to obtain ab initio energy-dependent widths is difficult even for diatomic molecules. Our approach can thus provide an ab initio estimation of the DEA cross section when other more accurate approaches are computationally expensive or not available.
ACKNOWLEDGEMENT

This work was supported by the National Science Foundation Grant No. PHY-1806915.