ChemPhysChem

Research Article
doi.org/10.1002/cphc.202200108

Chemistry Europe
European Chemical Societies Publishing

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Origin of Resonant Character in the Electron Impact Two-Body Neutral-Fragmentation of Methane

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The observation of peaks in the threshold region of two-body neutral fragmentation of methane molecule, i.e., $CH_4 \rightarrow CH_3 + H$, by low energy electron (LEE) impact has been an enigma. The prevailing explanation that this resonant behavior is due to excitation energy transfer is unsatisfactory since this process is not expected to show peaks in the cross-sections unless there is the involvement of electron-molecule resonances. Our first-principles calculations now reveal that the observed peaks could be explained as due to the formation of negative ion resonances, which dominantly dissociate into two neutral fragments and a free-electron. This case of methane is a pointer to the possibility that such reactions contribute significantly to neutral radical production from molecules by LEE impact in comparison to dissociative electron attachment, and in general could play a significant role in electron-based chemical control.

Introduction

The low energy electron (LEE) impact fragmentation of small hydrocarbon molecules are of fundamental importance in understanding the origin and evolution of complex organic molecules in the universe.[1–3] Among the various LEE impact fragmentation channels, the near-threshold channels are the most interesting ones. They are rich sources of highly reactive molecular precursors for advanced molecules. However, the overlap between several fragmentation channels in the threshold region and the openshell radical fragments pose a great challenge to their experimental and theoretical studies.[4–10]

The LEE impact two-body neutral fragmentation of methane yielding CH_3 radical and atomic hydrogen, i.e.,

$$e^- + CH_4 \rightarrow CH_3^{\#} + H^{\kappa} + e^- \quad (1)$$

where # and κ represent the electronic states, has attracted considerable attention as the simplest fragmentation channel possible in the threshold region of the smallest hydrocarbon. Owing to its simplicity, this channel is often used as a prototype for simulating the LEE-impact neutral fragmentation in higher hydrocarbons and also serves as an avenue for testing the theoretical methods for more complex many-body fragmentation channels.[4–12] Moreover, in the recent report of LEE induced C–H activation, this channel is understood to be one route for observed reaction in condensed phase.[3] However, despite its apparent simplicity, many of the characteristics of the LEE impact two-body neutral fragmentation in methane and its derivatives have remained poorly understood.[13]

One of the most notable features of the LEE impact two-body fragmentation in methane is the observation of peaks in CH_3 production cross-section at ~9.6 eV and 11.5 eV incident electron energies.[4,5] Overlying a continuum in the cross-section for the production of CH_3, distinct signatures of the peaks are seen. The continuum part of the cross-section is due to direct electronic and vibrational excitation by the projectile electrons. The structures in the cross-sections are reminiscent of resonant behavior and due to their similarity to the photoabsorption and photodissociation cross-sections they have been attributed to the excitation of neutral molecule and its subsequent fragmentation:

$$\underbrace{e^-(\varepsilon) + CH_4}_{\text{excitation energy transfer}} \rightarrow \underbrace{CH_4^*}_{\text{excited state}} + e^-(\varepsilon - h\nu) \quad (2)$$
$$\downarrow$$
$$CH_3^{\#} + H^{\kappa}$$

However, unlike photoexcitation, electron impact excitation does not have a resonant character unless it involves the formation of a negative ion resonance state (NIRS), which is an autoionizing transient state state of the electron-molecule compound.[14,15] The obvious process of meeting this require-

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/cphc.202200108

An invited contribution to the Special Collection featuring the Theoretical Chemistry Symposium 2021.

ment is the well known dissociative electron attachment (DEA).[14,15] Here, free electron of particular energy gets attached to a molecule forming a negative ion resonance that may dissociate to give a negative ion and one or more neutral fragments. In the case of methane, this process is fairly well studied. H^- and CH_2^- have been found to be formed by DEA to methane.[16] The absolute cross-sections for their formation[17] and their momentum distribution[18,19] have also been measured. In principle, the H^- formation in DEA would correspond to the CH_3 production. The DEA in H^- channel takes place in a broad energy range, starting a little below 8 eV and extending up to 13 eV with its center at about 10 eV.[17] Momentum imaging of H^- has revealed the presence of at least two resonances; one around 9 eV and below and the second one mostly at 10 eV and above, each with distinctly different momentum distributions.[18]

One may be tempted to attribute the observed peaks in the CH_3 production cross-section to these DEA processes. However, the measured absolute DEA cross-sections of the H^- channel is more than a factor of 30 smaller than the CH_3 production cross-section observed at 9.6 eV.[17,4] The difference increases further at the 11.5 eV peak in the neutral production. Hence DEA cannot account for the observed resonant production of neutral CH_3.[17]

A recent study on electron scattering on CH_4 using R-matrix method has given electron impact two-body neutral fragmentation cross-section of CH_4 which shows very good agreement with the experimental cross-section after correcting for the overestimation of the vertical excitation energies (see Figure S13 in Ref. [12]). Although the theoretical method, i.e., R-Matrix matrix method, used in the computation inherently includes the NIRS states in the calculation, the remarkable agreement was attributed to fortuitousness by the authors. On the other hand, theoretical calculations that includes only the initially prepared excited states of neutral CH_4 molecule do not show any distinct resonance structures that appear in the experimental cross-section (see for e.g., Ref. [6]).

Thus we need to investigate another process that is resonant in character, but leads to dissociation of the molecule into neutral products. It may be noted that until recently, DEA was regarded as the only fragmentation channel possible following resonant capture. Hence, using the available depictions, the resonant character of the LEE impact neutral-fragmentation was argued to have originated through an excitation energy transfer from the LEE to the methane molecule, i.e., through an electron impact electronic excitation of the methane molecule.[4,6] The fact that the electronic excitation in methane always leads to its dissociation was also used in support of this argument. As pointed out above neither this nor DEA explains the observation satisfactorily. Considering this, we look at the possible role of the newly proposed bond breaking by catalytic electron (BBCE) in the present case. The BBCE has recently been proposed on the basis of theoretical *ab initio* studies on cyclo-electron elimination reactions.[20,21] Here, an electron is resonantly captured by a molecule following which it fragments into two or more neutral products and a free-electron. Like the DEA, BBCE is a very general electron induced chemical reaction. The only criterion is that the electron should autoionize as an open system-catalyst from the reaction center of the electron-molecule compound while the reaction proceed with the formation of the products.[20–25] Experimental evidence for this process has been reported very recently in the resonant production of CO_2 from formic acid.[26] Here we investigate the possible role of BBCE in explaining the observed resonant production of CH_3 radical using high-level *ab initio* electronic structure methods.

Considering the two-body fragmentation of methane yielding neutral CH_3 radical as an example, the BBCE and the DEA processes can be understood as follows. A LEE induced resonant fragmentation is initiated when the target molecule captures the LEE of a particular kinetic energy to form a long-lived electron-molecule compound state which is also known as a negative ion resonance state (NIRS).

$$\underbrace{e^- + CH_4}_{\text{resonant capture}} \rightarrow \underbrace{\{e^-\}[CH_4]}_{\text{NIRS}} \tag{3}$$

The creation of the NIRS is a vertical process, in general. If the potential energy surface of the NIRS is dissociative in nature, then the vertically created NIRS undergoes a uni-molecular elementary fragmentation reaction, which can be neutral (BBCE) or non-neutral (DEA) in nature.

$$\underbrace{\{e^-\}[CH_4]}_{\text{NIRS}} \rightarrow \text{Molecular fragmentation} \tag{4}$$

The fragmentations corresponding to DEA and BBCE proceed in the same way except for the fact that while the electron is consumed in the DEA process and is bound to one of the fragments,

$$\underbrace{\{e^-\}[CH_4]}_{\text{NIRS}} \rightarrow CH_3^{\#} + H^- \qquad \text{DEA (non neutral)} \tag{5}$$

in BBCE the electron is set free in the product side of the reaction.

$$\underbrace{\{e^-\}[CH_4]}_{\text{NIRS}} \rightarrow \underbrace{e^- + CH_3^{\#} + H^x}_{\text{autodetachment}} \qquad \text{BBCE (neutral)} \tag{6}$$

Because of the apparent analogy with the open-system chemical catalysts such as photocatalysts and photoenzyme catalysts, the LEE in the BBCE reaction is termed as catalytic electron.[20–24] In this paper, using ab initio quantum chemical calculation, we study the role of the BBCE mechanism in the two body neutral dissociation of methane. The following sections provide a brief description of the calculation methods, results, discussion and conclusions.

Computational Methods

Recent advances in *ab initio* electronic structure methods have brought about a substantial improvement in the capability to

predict the molecular mechanism of LEE impact resonance processes in terms of well defined electronic potential energy surfaces corresponding to the NIRSs.[27–29] Of particular note is the recent introduction of continuum remover methods.[28,29] We used the real- and the complex-valued continuum remover potentials in conjunction with *ab initio* quantum chemical methods to compute the energy and autoionization decay rates of NIRS. The molecular quantum mechanical method we use herein has been described in much detail previously.[28,29] The working principle underlying this method can be understood as follows. The NIRS wavefunction is a scattering solution and can be viewed as a bound state coupled to the autoionization continuum. Adding a real-valued continuum remover potential, which does not support the continuum, to the non-interacting asymptote of the physical Hamiltonian removes the outgoing part of the continuum wavefunction contributing to the NIRS wavefunctions, which are thereby converted into a bound eigenstate.[27,29,30] Therefore, all the bound state quantum chemical methods can be used in conjunction with the real-valued continuum remover method for computing NIRS. The equation-of-motion coupled cluster singles and doubles (EA-EOMCCSD) method available in the GAMESS-US quantum chemical package[31] is modified and used for computing the electronic energy of the NIRS. An atom-centered aug-cc-pVTZ basis set augmented with a diffuse set of *s* and *p* type even-tempered primitive Gaussian functions is used for the EA-EOMCCSD calculation. The essential computational details pertaining to the potential energy and autoionization decay rate calculations and a discussion on the results of autoionization decay rate are included in the Supporting Information. In order to investigate the resonance capture mechanism in methane, we search for NIRS which are dissociative in nature. The potential energy curves of all NIRS below 14 eV are computed for the simplest two-body dissociation path imaginable, i.e., the collinear separation of a hydrogen atom from the methane molecule. We have used a C_s point group for the collinear separation path.

Results and Discussion

Our computational results are summarized in Figure 1. In Figure 1a, the *A*'' symmetry NIRSs contributing to a barrierless neutral fragmentation channel is shown in red color. This channels is followed on the adiabatic NIRSs potential energy curves. To minimize clutter in the figure, only the channel that is followed is shown. For an enlarged view and details of the potential energy curves contributing to this dissociation channel, see Figure 1 in the Supporting Information. At the equilibrium geometry, a one-particle (*1p*) NIRS contributes to this reaction path. The creation of this NIRS is due to the resonance capture of near 12 eV electron by the methane molecule. This is a vertical process and is represented by a wavy up-arrow. The orbital responsible for the resonant capture of the electron is having a strong Rydberg character and, hence, we term such orbitals as Rydberg-like orbitals (see also Ref. [12] for Rydberg-like orbitals of methane). The hybridized atomic orbitals from the higher shell of carbon atom contributes mostly to the Rydberg-like molecular orbital as seen in Figure 2c. The Rydberg-like orbital also possesses significant valence character inside the interaction region, i.e, high one-electron density inside the interaction region. In Figure 2c, two different iso-electron density surfaces of the Rydberg-like orbital are given to show its valence character and its nodal structure. Because of the strong valence character, the resonant creation of the

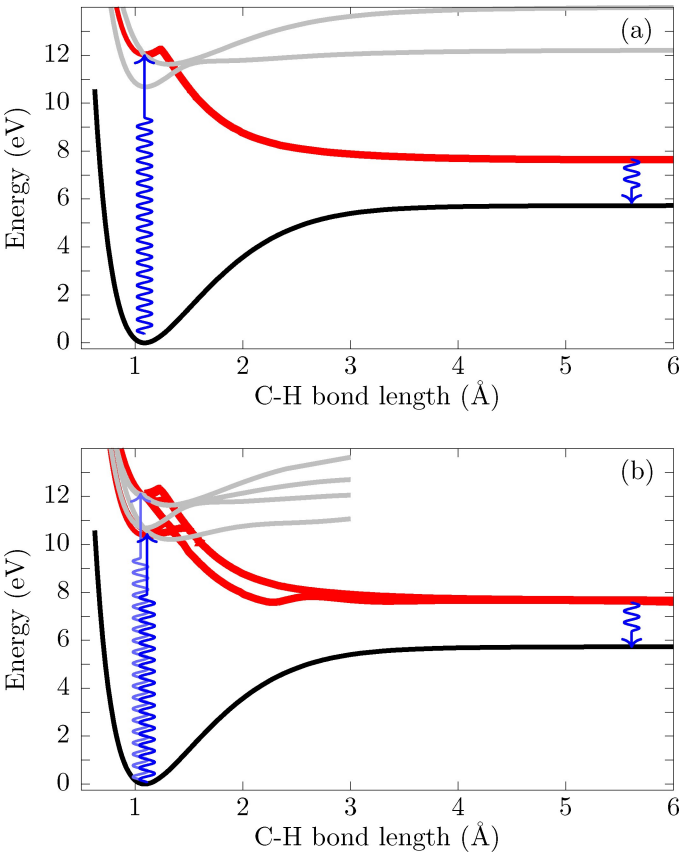

Figure 1. (**a**) The NIRS of *A*'' symmetry along the collinear fragmentation path for the separation of an H atom from CH_4 is shown in red color. The ground state and the excited states potential energy curves of the neutral CH_4 molecule are shown in black color and gray color, respectively. While the wavy up-arrows represent the resonance capture process by the methane molecule in its ground state equilibrium geometry, the wavy down-arrow represents the autodetachment of an electron from the asymptote of the fragmentation channel. (**b**) The NIRSs of A′ symmetry contributing to the LEE impact neutral fragmentation.

corresponding one-particle NIRS can induce and initiate nuclear dynamics. Further, in the Frank-Condon region, along the collinear separation path, the *1p*-NIRS crosses with a two-particle one-hole (*2p1h*) NIRS, where the crossing point is around ~0.15 Å away from the equilibrium geometry. The *2p1h*-NIRS is created by the HOMO (Figure 2a) and LUMO (Figure 2b) of the methane molecule within which the HOMO is occupied with one electron and LUMO is occupied with two electrons. One may note that these are the leading orbital contributions to the electron-attached states where the contributions are obtained from the wavefunction analysis within the *ab initio* method that computes the resonance attachment. This *2p1h*-NIRS is dissociative along the two-body collinear separation path. Towards the dissociation limit, the electronic configuration of the *2p1h*-NIRS is formed by the three singly occupied molecular orbitals, i.e., σ, σ^* and the non-bonding $3p_y$, which are shown in Figure 2(d–f).

The three-electron configuration corresponding to the *2p1h*-NIRS can be localized into a *1p*-NIRS of CH_3 radical and a radical hydrogen atom.

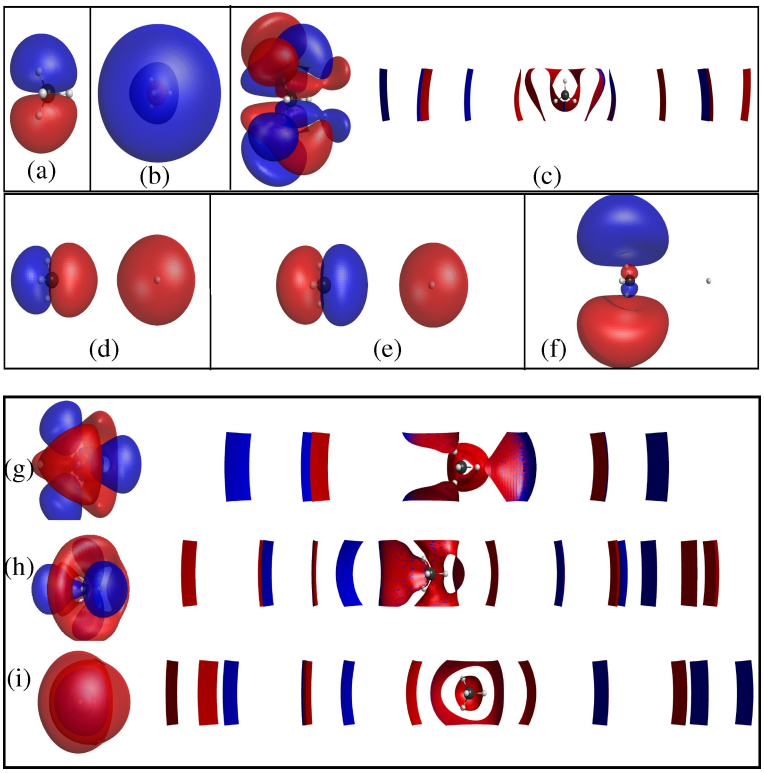

Figure 2. (**a**–**c**) The HOMO, LUMO, and the Rydberg-like orbitals of CH_4 at its equilibrium geometry, respectively. A cross-section of the Rydberg-like orbital for a small iso-surface value (10^{-6}) is also given, where the color change represents a node. The Rydberg-like orbital is responsible for the resonance capture process. The HOMO and LUMO contributes to the *2p1h*-NIRS in the Frank-Condon region. (**d**–**f**) The orbitals that contribute to the autodetachment of an electron from the *2p1h*-NIRS towards asymptote of the fragmentation channel, i.e., σ, σ^* and $^3P_{yC}$ orbitals as given in Eq. 7, are shown. (**g**–**i**) The one-particle orbitals that are responsible for the resonance capture of a near 10 eV electron.

$$\underbrace{\{e^-\}[CH_3...H]}_{\text{NIRS}}\underbrace{\{\sigma^1_{(2p_{zC}+1s_H)}\sigma^{*1}_{(2p_{zC}-1s_H)}3p^1_{yC}\}}_{\text{2p−1h configuration}} \downarrow \underbrace{\{e^-\}[CH_3]}_{\text{NIRS}}\underbrace{\{2p^1_{zC}3p^1_{yC}\}}_{\text{1p configuration of NIRS}} + H\{1s^1_H\} \quad (7)$$

Table 1. Energy position of resonances (units in eV) (see Table 1 in Supporting Information).

Experiment	Theory
11.5 (Ref. [4])	11.78
~9.6 (Ref. [4])	9.89

This essentially means that an electron autodetach from the NIRS of the CH_3 moiety. The wavy down-arrow represents the autodetachment of the electron from the CH_3 moiety.

The *A*' state near 12 eV that degenerates with the corresponding *A*'' states also displays a similar two-body neutral fragmentation, which are shown in Figure 1b. In addition to fragmentation channels originating near 12 eV, Figure 1b also reveals a fragmentation channel near 10 eV, where the one-particle NIRS crosses with the *2p1h*-NIRS at a point around ~ 0.25 Å away from the equilibrium geometry. The *1p*-NIRS responsible for the fragmentation has a contribution from three low energy Rydberg-like orbitals, which are shown in Figure 2(g–i). The computed resonance position are given in Table 1.

For a qualitative understanding of the competitiveness of the electron-induced reaction against the autdetachment process, we have computed the autodetachment decay rate (Γ, i.e., the inverse lifetime) of two NIRS. The resonance width is computed using the continuum remover complex absorbing potential within the framework of a determinant based CI method.[28] This method adds a complex valued potential to the non-interacting asymptote of the physical Hamiltonian. The resulting Hamiltonian has complex eigenvalues. The complex stabilized eigenvalues – stabilized against the variation of the potential strength – correspond to the resonance states, where their real part is the energy position and the imaginary part corresponds to the half width of the resonance state. For the computational details regarding this approach, see Supporting Information. The computed autodetachmnet rates are given in Tables 2 and 3. The χ_t is the non-interacting asymptotic point at which a complex potential is applied for absorbing the autodetaching electron. Although we have taken a large interaction region, because of the Rydberg character, we did not get good convergence of the autoionization decay rate with respect to χ_t. Hence, the width are presented for two chosen values of χ_t, which gives a qualitative understanding of

Table 2. Autodetachment decay rate of one-particle (*1p*) negative ion resonances at the equilibrium geometry of methane.

Resonance	Energy position (eV) (Experiment)	$\Gamma(eV)$ ($\chi_t = 10$ *au*)	$\Gamma(eV)$ ($\chi_t = 15$ *au*)
First resonance	~9.6 (Ref. [4])	0.023	0.020
Second resonance	11.5 (Ref. [4])	0.044	0.035

Table 3. Autodetachment decay rate of the two-particle one-hole (*2p1h*) negative ion resonances at 3 Å of C–H bond separation.

Resonance	Energy position (eV) (Experiment)	$\Gamma(eV)$ ($\chi_t = 10$ *au*)	$\Gamma(eV)$ ($\chi_t = 15$ *au*)
First resonance	~9.6 (Ref. [4])	0.016	0.014
Second resonance	11.5 (Ref. [4])	0.021	0.018

the results. The resonance width at the equilibrium geometry can can tell us whether the nuclear dynamics leading to fragmentation can be initiated or not. Since, the hydrogen elimination reactions are known to compete even with the faster autoionization process,[32] the reaction we discuss here is very likely to occur through the NIRS. The energy position of the reaction path above the autoionization threshold and the non-zero width at the large internuclear separations (Table 3) confirm the BBCE mechanism.

The mechanism of LEE impact two-body neutral fragmentation can be summarized as follows. The two-body neutral fragmentation is initiated by the resonance electron capture (near 12 eV or near 10 eV) into the Rydberg-like type molecular orbital of methane. During the course of the two-body fragmentation, an electron is autodetached from the one-particle NIRS of the CH_3 moiety. Although nonresonant excitation to the dissociative excited states of the neutral molecule can also cause neutral fragmentation, the steep descending character which seen in the dissociative negative ion resonance states is absent in the neutral states (see Figure 1a and 1b).

It is also noteworthy to mention that CH_3^- has not been observed in electron impact experiments so far. CH_3 has been found to have a very small positive electron affinity of 80 meV.[33] Though CH_3^- has been shown to have pyramidal structure,[34] the small electron affinity may not allow it to survive against autodetachment beyond picosecond time scale when the inevitable structural changes following H abstraction from the negative ion resonance of CH_4. Pump-probe experiments with picosecond time resolution in LEE impact experiments in the future may help to unravel such dynamics.

Conclusions

To conclude, we have put forwarded a more realistic explanation based on the recently discovered process of BBCE, for the peaks observed in the CH_3 production from methane at the threshold region as against the electron impact excitation mechanism believed to be responsible. The DEA process present in this energy region has a too low cross-section to be responsible for these peaks. Our *ab initio* electronic structure calculations reveal that resonance capture mechanism operative in this region dominantly decays into two-body neutral fragmentation of methane and a free-electron. Based on these results, we believe that the BBCE may be operative in a wider range of systems and with far more efficiency in creating radicals than DEA. Functional group dependence in DEA has been found to lead to site-selective fragmentation of molecules[35] allowing chemical control. The efficiency of this is decided by the absolute cross-sections for various DEA channels.[36] The present example of methane shows that the resonant attachment leads to larger possibility of producing fragments through BBCE than through DEA. It is important to note that there are very few experimental data on the pure neutral dissociation channels, due to the difficulties in detecting them. The possibility that like DEA, BBCE may also lead to site-selective fragmentation and thus could be an important tool in controlling chemical reactions using low energy electrons highlights the need for increased efforts at measuring the neutral dissociation cross sections for molecules. The observed features in the reaction yields in LEE based C–H activation[3] similar to that in the neutral dissociation of CH_4 indicate rich possibilities of role of BBCE in such reactions.

Supplementary Material

See supplementary material for the details regarding the *ab initio* quantum chemical computation of the negative ion resonance states.

Acknowledgment

E. K. gratefully acknowledges Raja Ramanna Fellowship during the course of this work.

Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: bond breaking by catalytic electron · low energy electron · neutral fragmentation · resonant electron attachment · coupled cluster calculations

[1] N. J. Mason, B. Nair, S. Jheeta, E. Szymańska, *Faraday Discuss.* **2014**, *168*, 235–247.
[2] T. N. V. Karsili, M. A. Fennimore, S. Matsika, *Phys. Chem. Chem. Phys.* **2018**, *20*, 12599–12607.

[3] S. Kundu, V. S. Prabhudesai, E. Krishnakumar, *J. Phys. Chem. C* **2017**, *121*, 22862–22871.
[4] C. Makochekanwa, K. Oguri, R. Suzuki, T. Ishihara, M. Hoshino, M. Kimura, H. Tanaka, *Phys. Rev. A* **2006**, *74*, 042704.
[5] C. Makochekanwa, M. Hoshino, H. Tanaka, M. Kimura, *J. Phys. Conf. Ser.* **2007**, *86*, 012004.
[6] M. Zółkowski, A. Vikár, M. L. Mayes, A. Bencsura, G. Lendvay, G. C. Schatz, *J. Chem. Phys.* **2012**, *137*, 22A510.
[7] D. A. Erwin, J. A. Kunc, *Phys. Rev. A* **2005**, *72*, 052719.
[8] M.-Y. Song, J.-S. Yoon, H. Cho, Y. Itikawa, G. P. Karwasz, V. Kokoouline, Y. Nakamura, J. Tennyson, *J. Phys. Chem. Ref. Data* **2015**, *44*, 023101.
[9] M. Fuss, A. Muñoz, J. Oller, F. Blanco, M.-J. Hubin-Franskin, D. Almeida, P. Limão-Vieira, G. García, *Chem. Phys. Lett.* **2010**, *486*, 110–115.
[10] A. Gadoum, D. Benyoucef, *IEEE Trans. Plasma Sci.* **2019**, *47*, 1505–1513.
[11] D. A. Erwin, J. A. Kunc, *J. Appl. Phys.* **2008**, *103*, 064906.
[12] W. J. Brigg, J. Tennyson, M. Plummer, *J. Phys. B* **2014**, *47*, 185203.
[13] M. B. Kiataki, M. T. do N Varella, M. H. F. Bettega, F. Kossoski, *J. Phys. Chem. A* **2020**, *124*, 8660–8667.
[14] D. G. Truhlar (d.), *Resonances in electron-molecule scattering, van der Waals complexes, and reactive chemical dynamics*, American Chemical Society, Division of Physical Chemistry, Washington DC, **1984**.
[15] I. I. Fabrikant, S. Eden, N. J. Mason, J. Fedor, Vol. 66 of *Advances In Atomic, Molecular, and Optical Physics*, E. Arimondo, C. C. Lin, S. F. Yelin (ds.), Academic Press, **2017**, pp. 545–657.
[16] T. E. Sharp, J. T. Dowell, *J. Chem. Phys.* **1969**, *50*, 3024.
[17] P. Rawat, V. S. Prabhudesai, M. A. Rahman, N. Bhargava Ram, E. Krishnakumar, *Int. J. Mass Spectrom.* **2011**, *277*, 96–102.
[18] N. B. Ram, E. Krishnakumar, *Chem. Phys. Lett.* **2011**, *511*, 22–27.
[19] N. Douguet, D. S. Slaughter, H. Adaniya, A. Belkacem, A. E. Orel, T. N. Rescigno, *Phys. Chem. Chem. Phys.* **2015**, *17*, 25621–25628.
[20] D. Davis, V. P. Vysotskiy, Y. Sajeev, L. S. Cederbaum, *Angew. Chem. Int. Ed.* **2011**, *50*, 4119–4122; *Angew. Chem.* **2011**, *123*, 4205–4208.
[21] D. Davis, V. P. Vysotskiy, Y. Sajeev, L. S. Cederbaum, *Angew. Chem. Int. Ed.* **2012**, *51*, 8003–8007; *Angew. Chem.* **2012**, *124*, 8127–8131.
[22] D. Davis, Y. Sajeev, *Phys. Chem. Chem. Phys.* **2016**, *18*, 27715–27720.
[23] D. Davis, Y. Sajeev, *J. Chem. Phys.* **2017**, *146*, 081101.
[24] D. Davis, K. G. Bhushan, Y. Sajeev, L. S. Cederbaum, *J. Phys. Chem. Lett.* **2018**, *9*, 6973–6977.
[25] D. Davis, Y. Sajeev, *Chem. Commun.* **2020**, *56*, 14625–14628.
[26] D. Davis, S. Kundu, V. S. Prabhudesai, Y. Sajeev, E. Krishnakumar, *J. Chem. Phys.* **2018**, *149*, 064308.
[27] Y. Sajeev, A. Ghosh, N. Vaval, S. Pal, *Int. Rev. Phys. Chem.* **2014**, *33*, 397–425.
[28] Y. Sajeev, V. Vysotskiy, L. S. Cederbaum, N. Moiseyev, *J. Chem. Phys.* **2009**, *131*, 211102.
[29] Y. Sajeev, *Chem. Phys. Lett.* **2013**, *587*, 105–112.
[30] Y. Sajeev, M. Thodika, S. Matsika, *J. Chem. Theory Comput.* **2022**, *18*, 2863–2874, doi:10.1021/acs.jctc.1c01096.
[31] J. R. Gour, P. Piecuch, *J. Chem. Phys.* **2006**, *125*, 234107.
[32] G. A. Gallup, *Phys. Rev. A* **2013**, *88*, 052705.
[33] G. B. Ellison, P. C. Engelking, W. C. Lineberger, *J. Am. Chem. Soc.* **1978**, *100*, 2556–2558.
[34] D. S. Marynick, D. A. Dixon, *Proc. Natl. Acad. Sci. USA* **1977**, *74*, 410–413.
[35] V. S. Prabhudesai, D. Nandi, A. H. Kelkar, E. Krishnakumar, *Phys. Rev. Lett.* **2005**, *95*, 143202.
[36] V. S. Prabhudesai, D. Nandi, A. H. Kelkar, E. Krishnakumar, *J. Chem. Phys.* **2008**, *128*, 154309.

Manuscript received: February 15, 2022
Revised manuscript received: May 4, 2022
Accepted manuscript online: May 4, 2022
Version of record online: May 30, 2022