

Oscillator strength study of the excitations of valence-shell of C_2H_2 by high-resolution inelastic x-ray scattering

Qiang Sun(孙强), Ya-Wei Liu(刘亚伟), Yuan-Chen Xu(徐远琛), Li-Han Wang(王礼涵), Tian-Jun Li(李天钧), Shu-Xing Wang(汪书兴), Ke Yang(杨科), and Lin-Fan Zhu(朱林繁)

Citation: Chin. Phys. B, 2022, 31 (**5**): 053401. DOI: 10.1088/1674-1056/ac422e
Journal homepage: http://cpb.iphy.ac.cn; http://iopscience.iop.org/cpb

What follows is a list of articles you may be interested in

Vibrational effects on electron momentum distributionsof outer valence orbitals of benzene

Yu Zhang(张钰), Shanshan Niu(牛珊珊), Yaguo Tang(唐亚国), Yichun Wang(王忆纯), Xu Shan(单旭), Xiangjun Chen(陈向军)

Chin. Phys. B, 2020, 29 (**2**): 023402. DOI: 10.1088/1674-1056/ab671b

Differential cross sections for electron impact excitation of molecular hydrogen using the momentum-space multichannel optical method

Yuan-Cheng Wang(王远成), Jia Ma(马佳), Ya-Jun Zhou(周雅君)

Chin. Phys. B, 2016, 25 (**4**): 043401. DOI: 10.1088/1674-1056/25/4/043401

Formation of hydrogen atom in 2s state in proton-sodium inelastic scattering

Sabbah A. Elkilany

Chin. Phys. B, 2015, 24 (**3**): 033402. DOI: 10.1088/1674-1056/24/3/033402

Assessment of delocalized and localized molecular orbitals through electron momentum spectroscopy

Liu Yuan, Cheung Ling-Fung, Ning Chuan-Gang

Chin. Phys. B, 2014, 23 (**6**): 063403. DOI: 10.1088/1674-1056/23/6/063403

Decay pathways of superexcited states of nitrous oxide

Lin Mei, Liu Ya-Wei, Zhong Zhi-Ping, Zhu Lin-Fan

Chin. Phys. B, 2014, 23 (**5**): 053403. DOI: 10.1088/1674-1056/23/5/053403

Oscillator strength study of the excitations of valence-shell of C_2H_2 by high-resolution inelastic x-ray scattering

Qiang Sun(孙强)[1], Ya-Wei Liu(刘亚伟)[2], Yuan-Chen Xu(徐远琛)[1], Li-Han Wang(王礼涵)[1], Tian-Jun Li(李天钧)[1], Shu-Xing Wang(汪书兴)[1], Ke Yang(杨科)[3,†], and Lin-Fan Zhu(朱林繁)[1,‡]

[1] *Hefei National Research Center for Physical Sciences at Microscale and Department of Modern Physics, University of Science and Technology of China, Hefei* 230026, *China*

[2] *Anhui Province Key Laboratory of Medical Physics and Technology, Institute of Health and Medical Technology, Hefei Institutes of Physical Science, Chinese Academy of Sciences, Hefei* 230026, *China*

[3] *Shanghai Advanced Research Institute, Chinese Academy of Sciences, Shanghai* 201204, *China*

(Received 22 October 2021; revised manuscript received 30 November 2021; accepted manuscript online 11 December 2021)

The oscillator strengths of the valence–shell excitations of C_2H_2 are extremely important for testing theoretical models and studying interstellar gases. In this study, the high-resolution inelastic x-ray scattering (IXS) method is adopted to determine the generalized oscillator strengths (GOSs) of the valence–shell excitations of C_2H_2 at a photon energy of 10 keV. The GOSs are extrapolated to their zero limit to obtain the corresponding optical oscillator strengths (OOSs). Through taking a completely different experimental method of the IXS, the present results offer the high energy limit for electron collision to satisfy the first Born approximation (FBA) and cross-check the previous experimental and theoretical results independently. The comparisons indicate that an electron collision energy of 1500 eV is not enough for C_2H_2 to satisfy the FBA for the large squared momentum transfer, and the line saturation effect limits the accuracy of the OOSs measured by the photoabsorption method.

Keywords: C_2H_2, inelastic x-ray scattering, dynamic parameters

PACS: 34.80.Gs, 61.05.cf, 95.30.Ky **DOI:** 10.1088/1674-1056/ac422e

1. Introduction

As an important astronomical molecule, C_2H_2 exists widely in interstellar medium,[1] carbon stars,[2,3] and planetary atmospheres.[4,5] So it is crucial for scientists to identify and determine the abundances of C_2H_2 in space, which is very helpful for establishing the theory of element origin and studying the evolution of celestial bodies. One key factor to extract the abundance information of matter from the astronomically observed spectra is the high-precision atomic and molecular dynamic parameters, including C_2H_2. For instance, C_2H_2 was identified in the Shaula transmission spectrum from the Cassini UVIS FUV spectrograph,[5] based on the observation of the R30–R32 transitions. In addition, C_2H_2 is one of the simplest polyatomic molecules, and it plays a big part in burning processes as well. Therefore, benchmark physical quantities including the oscillator strengths and cross sections of the valence–shell excitations (VSEs) of C_2H_2 are vital for fundamental research as well as for understanding plenty of astrophysical and photochemical processes.

Since Price[6] observed the first discrete photoabsorption spectrum of C_2H_2, extensive experimental and theoretical researches on the photoabsorption cross section of C_2H_2 were reported[7–13] and well summarized by Liu *et al.* recently.[7] Most previous studies[8–13] are the photoabsorption measurements based on the Bear–Lambert law, with various experimental conditions, *e.g.*, different energy resolutions, target pressures, and interaction lengths. Due to the well-known line saturation effect (LSE), the OOS (equivalent to the integral photoabsorption cross section) measured by the photoabsorption method for the discrete state is lower than its true value, especially for the intense and narrow transitions.[14–16] So the dipole (e,e) method[17] and the extrapolation method[7] were also used to determine the OOSs of C_2H_2, which are not affected by the LSE. It ought to be mentioned that recently the dipole (γ,γ) method[15,16,18,19] is proposed to measure the OOSs without the influence of the LSE. Furthermore, the OOSs of C_2H_2 were calculated by the state averaged, complete active space MCSCF, multireference CI method,[20] and the LCAO-MO-SCF method,[21] but limited to the R30, R31, and R32 states. It should be emphasized that the available experimental and theoretical OOSs of C_2H_2 show apparent discrepancies, and a further investigation is meaningful.

Compared to the OOSs, the GOSs of the VSEs of C_2H_2 are much scarce, and the quantitative GOSs of C_2H_2 were only reported by Liu *et al.*[7] with an incident electron energy of 1.5 keV. Moreover, there is no theoretical GOS investigation of C_2H_2, to the best of our knowledge. So for the purpose of

†Corresponding author. E-mail: yangke@zjlab.org.cn
‡Corresponding author. E-mail: lfzhu@ustc.edu.cn

© 2022 Chinese Physical Society and IOP Publishing Ltd

making a cross-check to the GOSs obtained by the electron energy-loss spectroscopy (EELS), other independent experimental results are greatly recommended.

Recently, the high-resolution IXS has been applied to determine the atomic and molecular dynamic parameters,[16,22,23] which is a newly developed experimental technique based on the third-generation synchrotron radiation. Compared to the EELS method, IXS is a weak probe and not affected by the higher-order Born terms.[16,24,25] Therefore, the atomic and molecular dynamic parameters measured by IXS can serve as the high-energy limit of electron collision, and the high-energy EELS and theoretical results can be strictly cross-checked. In the current work, the GOSs of the VSEs of C_2H_2 were determined by the IXS at 10-keV photon energy. The corresponding OOSs were derived by extrapolating the GOSs to the zero limit of $q^2 \to 0$. For brevity, we use the term names, principal and vibrational quantum numbers to represent the corresponding vibronic states, *e.g.*, the vibronic state of $R'n = 3$, $v_2' = 0$ is marked as R′30 in this paper, and the CC stretch vibration mode dominates in the Rydberg series.[11,17] Furthermore, the vibronic transitions of the $\widetilde{E}$ state are represented as $\widetilde{E}0$–$\widetilde{E}5$, according to the works of Suto & Lee[11] and Cooper *et al.*[17]

2. Experimental method

This experiment was performed at the BL12XU station of SPring-8.[22,23] The incident photon energy is about 10 keV, and the experimental procedures employed have been elaborated in our previous works.[16,26,27] In brief, a monochromator of Si (333) and a spherical analyzer of Si (555) were respectively used to get an energy resolution of approximately 70 meV. In the experiment, the analyzer energy of the scattered photon is fixed at approximately 9890 eV, while the energy of incident photon changed, and the energy difference between them, *i.e.*, the so-called energy loss, equal the target's excitation energy. Then the excitation spectra at the scattering angles of 7°–50° were recorded. During the measurement, C_2H_2 and He were sealed in a gas cell by turns at pressures of 0.199 MPa and 0.903 MPa respectively, so as to absolutely calibrate the experimental data.

On the basis of Bethe theory,[28–30] the electronic structure determined by the initial and final states' wave functions is directly related to the GOS, which can be derived from the experimental differential cross sections (DCSs) obtained by the EELS under the FBA or the ones measured by the IXS:

$$f(\boldsymbol{q},\omega_n) = \frac{2\omega_n}{q^2}\left|\left\langle \Psi_n \left| \sum_{j=1}^{N} \exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_j) \right| \Psi_0 \right\rangle\right|^2 = \frac{2\omega_n}{q^2}\frac{1}{r_0{}^2}\frac{\omega_\mathrm{i}}{\omega_\mathrm{f}}\frac{1}{|\boldsymbol{\varepsilon}_\mathrm{i}\cdot\boldsymbol{\varepsilon}_\mathrm{f}^*|^2}\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_\gamma. \quad (1)$$

Here Ψ_0 and Ψ_n represent the initial and final wave functions of the specific atom or molecule, respectively. The summation is for all electrons and $\boldsymbol{r}_j$ is the j-th electron's position vector. $\left(\frac{\mathrm{d}\sigma}{\mathrm{d}\Omega}\right)_\gamma$ represents the DCS determined by the IXS. $f(\boldsymbol{q},\omega_n)$ is the GOS, while $\boldsymbol{q}$ and ω_n are respectively the moment transfer vector and the excitation energy. The factor $|\boldsymbol{\varepsilon}_\mathrm{i}\cdot\boldsymbol{\varepsilon}_\mathrm{f}^*|^2$ derives from the incident and scattered photons' polarized directions. r_0 is the classical electron radius, while ω_i and ω_f are the energies of the incident and scattered photons, respectively.

Figure 1 shows a typical IXS spectrum of C_2H_2 at 7°, where the VSEs of the C_2H_2 are assigned according to the work of Suto & Lee.[11] The individual intensities of the excitations in 8.00 eV–10.07 eV were obtained by the least-squares fitting method. In the fitting procedures, the excitations in 8.9 eV–10.07 eV are fitted with the same Gaussian peak profile and their energies are taken from Ref. [17] and fixed. For the vibronic states of R30, R31, and R32, they are well separated from other transitions and variable widths are used due to their predissociation nature. Since the present energy resolution of 70 meV is not enough to separate the closely nearby transitions, the sum GOSs for the excitations of $\sum_{j=0}^{2}\widetilde{E}j + \mathrm{R}'30 + \mathrm{R}'''30$, $\sum_{j=3}^{5}\widetilde{E}j + \mathrm{R}'31 + \mathrm{R}'''31$, $\mathrm{R}'32 + \mathrm{R}'''32$, and $\mathrm{R}40 + \mathrm{R}''40$ (they are called as F1, F2, F3, and F4 in the following text for conciseness) are given, to avoid the larger experimental uncertainties of random allocation of intensities. The main sources of the present experimental uncertainties are the statistical counts, the fitting process, and the normalizing procedure, as shown in the corresponding tables and figures.

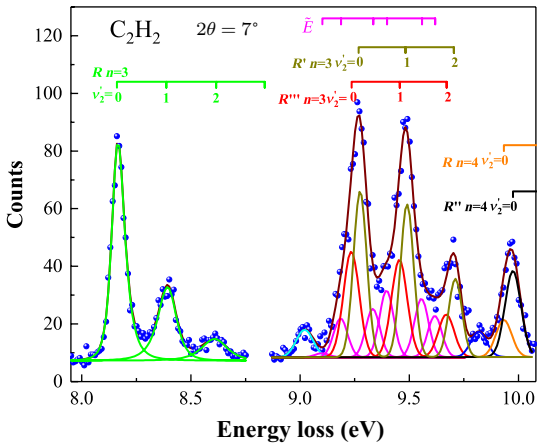


Fig. 1. A typical IXS spectrum of the valence–shell excitations of C_2H_2. The dots are the experimental data while the solid lines are the fitted curves.

3. Results and discussion

The present IXS GOSs of the VSEs of C_2H_2 are given in Table 1 and shown in Fig. 2, together with the previous EELS results of Liu *et al.*[7]

Table 1. The GOSs of the valence–shell excitations of C_2H_2. The data are multiplied by a factor of 10^3. Data in the parentheses are the experimental uncertainties.

q^2 (a.u.)	R30	R31	R32	F1	F2	F3	F4
0.11	75(9)	37(3)	15(3)	133(14)	144(10)	43(5)	50(6)
0.21	37(5)	20(2)	8.4(1.7)	93(9)	87(6)	24(3)	24(3)
0.39	15(2)	7.3(0.6)	2.7(0.6)	66(7)	62(4)	17(2)	18(2)
0.69	2.1(0.4)	1.0(0.1)	0.69(0.19)	25(3)	26(2)	5.6(0.8)	6.7(0.9)
1.22	0.68(0.14)	0.43(0.06)	0.03(0.02)	8.5(1.0)	7.7(0.7)	1.6(0.3)	2.0(0.3)
2.15	1.5(0.3)	1.5(0.1)	0.82(0.20)	1.2(0.2)	1.2(0.2)	0.21(0.07)	1.4(0.2)
3.30	0.81(0.16)	1.1(0.1)	0.70(0.18)	0.82(0.16)	1.1(0.2)	0.25(0.08)	1.1(0.2)
5.04	0.41(0.10)	0.37(0.06)	0.12(0.05)	–	–	–	–

Table 2. The OOSs of the valence–shell excitations of C_2H_2. The data are multiplied by a factor of 10^3. Data in the parentheses are the corresponding experimental uncertainties.

	R30	R31	R32	F1	F2	F3	F4
Present OOSs	122.1(9.8)	59.0(4.7)	19.3(3.8)	168.4(27.9)	200.9(14.2)	62.7(5.7)	60.3(9.2)
Electron impact							
Ref. [7]	106.2(7.7)	55.1(3.0)	16.9(1.8)	161.7(8.2)	189.7(10.6)	54.7(5.5)	76.4(6.9)
Ref. [17]	105.2(10.5)	53.3(5.3)	16.4(1.6)	161.0(16.1)	185.5(18.6)	53.4(5.3)	76.0(7.6)
Photoabsorption							
Ref. [8]	101.0(10.1)	41.0(4.1)	8.0(0.8)	–	–	–	–
Ref. [9]	85.9(8.6)	42.5(4.3)	8.7(0.9)	–	–	–	–
Ref. [10]	85.0(8.5)	41.4(4.1)	8.5(1.0)	–	–	–	–
Ref. [11]	78.5	33.3	9.2	–	–	38.2	51.2
Ref. [12]	74.3	30.6	4.6	–	–	–	–
Ref. [13]	61.6	–	–	–	–	–	22.9
Theoretical calculation							
Ref. [20]	104.6	40.8	9.4	–	–	–	–
Ref. [21]	72.0	–	–	–	–	–	–

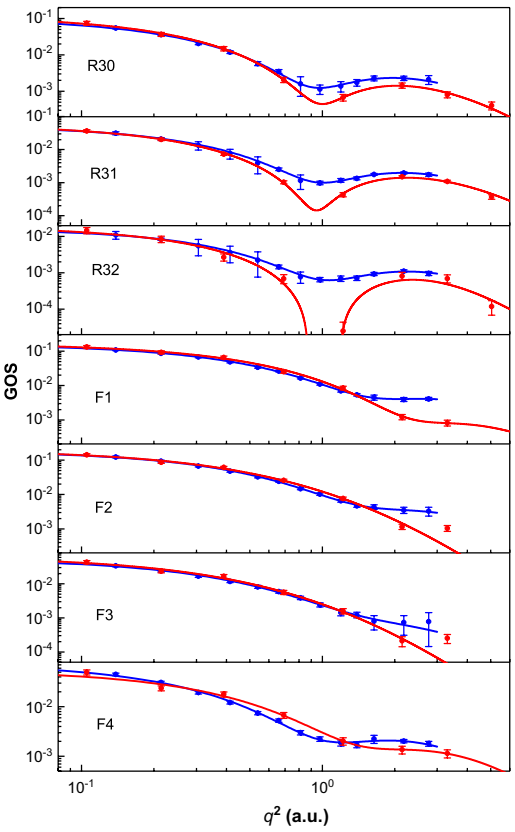


Fig. 2. Present GOSs of R30, R31, R32, F1, F2, F3, and F4 excitations of C_2H_2 obtained by IXS (red), together with previous EELS (blue) results. The dots are the experimental results, while the solid lines are their fitted curves using Lassettre formula.[31]

It is obvious in Fig. 2 that all GOSs show a similar trend, *i.e.*, decreasing with the q^2 in the small q^2 region, which is the typical behavior of the dipole allowed transitions. Furthermore, all GOSs of R30, R31, and R32 measured by these two methods are very consistent in $q^2 < 0.5$ a.u. and have a minimum at about 1 a.u. The EELS GOSs around the minimum are significantly larger than the IXS ones, which may be caused by the failure of the FBA in the EELS, since the FBA is always valid in the IXS.[16] Similarly, the IXS and EELS GOSs of the features of F1–F4 are also in excellent consistence in $q^2 < 1$ a.u., while the EELS GOSs are apparently larger than the IXS ones in $q^2 > 1$ a.u. The reason for this phenomenon should be the same as the one of the R30, R31, and R32, *i.e.*, the failure of the FBA in the EELS, although a collision electron energy of up to 1500 eV has been used.

Using the famous Lassettre formula,[31] the OOSs are determined by extrapolating the corresponding GOSs to the zero limit of $q^2 \to 0$, which are given in Table 2 and shown in Fig. 3, where the previous experimental and theoretical results are also listed and exhibited.

It is obvious that the present OOSs of all excitations agree well with the extrapolated OOSs obtained by the EELS method[7] and the dipole (e,e) ones,[17] while they are larger than the photoabsorption ones on the whole. This phe-

nomenon can be attribute to the LSE, although it is expected to be weak for the VSEs of C_2H_2 due to its predissociation nature. So the present OOSs as well as the extrapolated and dipole (e,e) ones are more reliable. As for the theoretical calculations, it is easy to find in Fig. 3(c) that the theoretical results are smaller than the reliable experimental results. It seems that at present stage it is hard to calculate accurate OOSs for the polyatomic molecules such as C_2H_2.

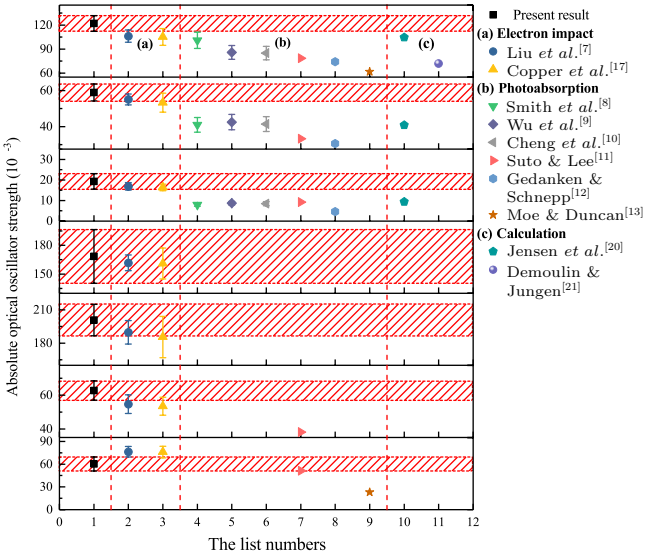


Fig. 3. Present OOSs of the R30, R31, R32, F1, F2, F3, and F4 excitations of C_2H_2 from top to bottom, along with the previous ones.

4. Summary and conclusion

In this work, the GOSs of the R30, R31, R32, F1, F2, F3, and F4 transitions of C_2H_2 have been measured by high-resolution IXS. It is found that the present IXS GOSs are in good agreement with the previous EELS results in small q^2 region, while the discrepancies between them become larger as q^2 increases, especially around the GOS minima for R30, R31, and R32, which may be due to the failure of the FBA in the EELS. Through extrapolating the GOSs to the zero limit of q^2, the OOSs of the VSEs of C_2H_2 have been obtained. The comparison shows that the previous photoabsorption measurement suffers from the LSE. The present IXS GOSs and OOSs cross-check the previous experimental and theoretical results independently, and give a deep insight to the excitation mechanism of C_2H_2.

Acknowledgments

We gratefully thank Nozomu Hiraoka for his help on the IXS experiment at SPring-8. Project supported by the Strategic Priority Research Program of the Chinese Academy of Science (Grant No. XDB34000000), the National Natural Science Foundation of China (Grant Nos. U1932207 and 12104437), and the National Key Research and Development Program of China (Grant No. 2017YFA0402300). The support from the Heavy Ion Research Facility in Lanzhou (HIRFL) is also acknowledged. The IXS experiment was performed at the BL12XU of SPring-8 with the approval of Japan Synchrotron Radiation Research Institute (Proposal No. 2019A4275) and "National" Synchrotron Radiation Research Center, Taiwan, China (Proposal No. 2019-2-089-1).

References

[1] Prasad S S and Huntress W T 1980 *Astrophys. J. Suppl. Ser.* **43** 1
[2] Ridgway S T, Hall D N B, Kleinmann S G, Weinberger D A and Wojslaw R S 1976 *Nature* **264** 345
[3] Jorgensen U G and Johnson H R 1991 *Astron. Astrophys.* **244** 462
[4] Mitchell G F, Prasad S S and Huntress W T 1981 *Astrophys. J.* **244** 1087
[5] Shemansky D E, Stewart A F, West R A, Esposito L W, Hallett J T and Liu X M 2005 *Science* **308** 978
[6] Price W C 1935 *Phys. Rev.* **47** 444
[7] Liu Y W, Xu L Q, Chen T, Qi D G, Xiong T and Zhu L F 2018 *Astrophys. J. Suppl. Ser.* **234** 10
[8] Smith P L, Yoshino K, Parkinson W H, Ito K and Stark G 1991 *J. Geophys. Res. Planets* **96** 17529
[9] Wu C Y R, Chen F Z and Judge D L 2001 *J. Geophys. Res. Planets* **106** 7629
[10] Cheng B M, Chen H F, Lu H C, Chen H K, Alam M S, Chou S L and Lin M Y 2011 *Astrophys. J. Suppl. Ser.* **196** 3
[11] Suto M and Lee L C 1984 *J. Chem. Phys.* **80** 4824
[12] Gedanken A and Schnepp O 1976 *Chem. Phys. Lett.* **37** 373
[13] Moe G and Duncan A B F 1952 *J. Am. Chem. Soc.* **74** 3136
[14] Chan W F, Cooper G and Brion C E 1991 *Phys. Rev. A* **44** 186
[15] Xu L Q, Liu Y W, Kang X, Ni D D, Yang K, Hiraoka N, Tsuei K D and Zhu L F 2015 *Sci. Rep.* **5** 18350
[16] Wang S X and Zhu L F 2020 *Matter Radiat. Extremes* **5** 054201
[17] Cooper G, Burton G R and Brion C E 1995 *J. Electron Spectrosc. Relat. Phenom.* **73** 139
[18] Xu L Q, Liu Y W, Xu X, Ni D D, Yang K and Zhu L F 2017 *Eur. Phys. J. D* **71** 183
[19] Xiong T, Xu Y C, Yang K, Hiraoka N and Zhu L F 2019 *Astrophys. J.* **885** 163
[20] Jensen J O, Adams G F and Chabalowski C F 1990 *Chem. Phys. Lett.* **172** 379
[21] Demoulin D and Jungen M 1974 *Theoret. Chim. Acta* **34** 1
[22] Xie B P, Zhu L F, Yang K, Zhou B, Hiraoka N, Cai Y Q, Yao Y, Wu C Q, Wang E L and Feng D L 2010 *Phys. Rev. A* **44** 032501
[23] Zhu L F, Wang L S, Xie B P, Yang K, Hiraoka N, Cai Y Q and Feng D L 2011 *J. Phys. B: At. Mol. Opt. Phys.* **44** 025203
[24] Platzman P M and Tzoar N 1965 *Phys. Rev.* **139** A410
[25] Eisenberger P and Platzman P M 1970 *Phys. Rev. A* **2** 415
[26] Kang X, Yang K, Liu Y W, Xu W Q, Hiraoka N, Tsuei K D, Zhang P F and Zhu L F 2012 *Phys. Rev. A* **86** 022509
[27] Zhu L F, Xu W Q, Yang K, Jiang Z, Kang X, Xie B P, Feng D L, Hiraoka N and Tsuei K D 2012 *Phys. Rev. A* **85** 030501
[28] Bethe H 1930 *Ann. Phys.* **397** 325
[29] Bethe H 1932 *Z. Phys.* **76** 293
[30] Inokuti M 1971 *Rev. Mod. Phys.* **43** 297
[31] Lassettre E N 1965 *J. Chem. Phys.* **43** 4479