Probing the delocalized core-hole via inner-shell excitation in $N_2$

Yuan-Chen Xu, Shu-Xing Wang*, Xiao-Jiao Du, Li-Han Wang and Lin-Fan Zhu*

Department of Modern Physics, University of Science and Technology of China, Hefei, Anhui 230026, People’s Republic of China

* Authors to whom the correspondence should be addressed.

E-mail: wangshuxing@ustc.edu.cn and lfzhu@ustc.edu.cn

Keywords: core-hole localization, inner-shell excitation, electron scattering, forbidden transition

Abstract

The dispute about whether the $1s$ core-hole is localized on one atom or delocalized over both in a homonuclear diatomic molecule has continued for decades, which has been extensively studied by the photoelectron and electron–ion coincidence spectroscopies. For $N_2$, if the $1s$ core-hole is delocalized, the K-shell excitation into the $1\pi_g$ orbital should split into two components, i.e., the dipole-allowed transition from the ungerade $1\sigma_u$ state and the dipole-forbidden transition from the gerade $1\sigma_g$ state. However, only the dipole-allowed transition has been observed up to now.

Here, we report the inner-shell electron energy loss spectra of $N_2$ at different scattering angles with an incident electron energy of 1500 eV and an energy resolution of 65 meV. The vibrational structures of both the dipole-allowed $(1\sigma_g)^{-1}(1\pi_g)^1$ and dipole-forbidden $(1\sigma_g)^{-1}(1\pi_g)^1$ states of $N_2$ have been identified at different momentum transfers. The splitting between the $(1\sigma_g)^{-1}(1\pi_g)^1$ and $(1\sigma_u)^{-1}(1\pi_u)^1$ states with the reverse symmetry is determined to be $67 \pm 7$ meV. Moreover, the momentum transfer dependence behavior of the transition intensity ratio agrees with the theoretical predictions, as increasing to a maximum and then decreasing. The experimental observations clearly show that the inner most electrons can be described by $1\sigma_g$ and $1\sigma_u$, which indicates that the inner-shell $1s$ core-hole of $N_2$ is delocalized over two N atoms based on the excitation process.

1. Introduction

The valence electrons in a homonuclear diatomic molecule are recognized as delocalized over both atoms. However, whether the inner-shell electron is localized on one atom or delocalized over both remains a controversial but attractive puzzle. Chemists and physicists have always considered that the orbital density of the inner-shell electron is confined near one nucleus, i.e., the overlap of their wave functions between the neighboring atoms is almost negligible [1]. This scenario of localized core-holes in homonuclear molecules was firstly proposed by Bagus and Schaefer [2] in the early 1970s, and their calculated ionization energy of $O_2$ with a localized core-hole agreed much better with experiment than symmetry-adapted core-hole calculation. However, a later investigation indicated that the inconsistency between the calculations with localized or delocalized core-hole can mostly be attributed to the electron–electron correlations [3]. The theoretically predicted and experimentally demonstrated gerade–ungerade core-hole splitting of about 97 meV in $N_2^+$ supports the delocalized picture [4–8]. Similar gerade–ungerade core-hole splitting were also observed in molecules $C_2H_2$ and $C_2D_2$ [9]. With the development of coincidence techniques, the angular distributions of photoelectrons, Auger electrons and ionic fragments in the molecular frame were used to study the localized or delocalized nature of the core-hole state. The symmetric photoelectron pattern of $N_2$ [8, 10] supports the delocalized picture. In contrast, the asymmetric patterns of photoelectrons and ionic fragments in $N_2$ [11], $O_2$ [12], $C_2H_2$ [13], Ne$_2$ [14], CF$_4$ [15] put the opposite view of a localized core-hole, while the vibronic effects may complicate the problem in polyatomic systems [16, 17]. However, the comprehensive studies by coincidence measurement of photoelectron, Auger electron and ionic fragments of $N_2$ [18] and $CS_2$ [19] indicate that observation of symmetry breaking (localization)
Figure 1. Scenarios for the inner-shell excitations in N2 with (a) delocalized or (b) localized core-hole. Note that only the dipole-allowed transition \(1s \sigma_u \rightarrow 1\pi_g\) is presented.

or preservation (delocalization) depends on the measurement, i.e., the photoelectron and Auger electron form an entangled pair. As pointed out by Ueda [20], the coincident angular correlation measurements can project the entire entangled wave function describing the photoemission to the localized or delocalized hole. The dispute for decades has been settled based on the photoionization process since then.

Note that the inner-shell excitation also creates a core-hole and the localized or delocalized picture will result in different transition scenarios. As sketched in figure 1, if the core-hole is delocalized, the inner-shell transition in N2 should split into the dipole-allowed \(1s \sigma_u \rightarrow 1\pi_g\) and dipole-forbidden \(1s \sigma_g \rightarrow 1\pi_g\). Otherwise, the transition should degenerate as \(1s \rightarrow 1\pi_g\). Therefore, synchrotron radiations [21, 22] and fast electrons [23, 24] have been applied to study the inner-shell excitations in N2 while only dipole-allowed transitions are observable with synchrotron radiations. The nearly identical term values, vibrational frequencies, and internuclear separations of the \(1s\)-excited states in N2 and the \(2\pi\)-excited states in NO, allow for a complete peak assignment for the Rydberg series of N2 and strongly supported both the core-hole localization picture and equivalent-core model [21]. The following measurement of the C 1s near-edge photoabsorption spectroscopy of C2H4 indicated the importance of vibronic coupling which provides a mechanism for localized core-hole [22]. However, electron impact method can detect not only the dipole-allowed but also the dipole-forbidden transitions, which can be used to probe the \((1s\sigma_g)^{-1}(1\pi_g)^1\) state if the core-hole is delocalized [25]. Note that measuring only the excitation processes leads to an incoherent sum of the gerade and ungerade core-hole states, i.e., the inner-shell excitations should include the dipole-allowed \((1s\sigma_u)^{-1}(1\pi_g)^1\) and dipole-forbidden \((1s\sigma_g)^{-1}(1\pi_g)^1\) components. In 1982, Shaw et al [24] intended to measure the vibrational structure of the inner-shell \((1s\sigma_g)^{-1}(1\pi_g)^1\) state in N2 at different incident electron energies. However, they failed to observe the forbidden component due to the limited statistical accuracy.

In this work, we report the high-resolution electron energy loss spectra of the inner-shell excitations in N2 measured at an angle-resolved electron energy loss spectrometer (EELS). The vibrational structure of the inner-shell \((1s\sigma)^{-1}(1\pi_g)^1\) state of N2 have been resolved at different scattering angles. The two components
of $1s\sigma_g \rightarrow 1\pi_g$ and $1s\sigma_u \rightarrow 1\pi_g$ are resolved in the spectra at different angles by the least-squares fitting. The energy splitting and intensity ratios between the two components as a function of the momentum transfers, as well as the relative Franck–Condon factors have been obtained. The paper is organized as follows. In section 2, the experimental method is presented with a detailed description of data analysis. The experimental results are discussed in section 3. Finally, we summarize the results as a conclusion in section 4.

2. Experiment and data analysis

The experiment was performed by employing an angle-resolved EELS, which has been described in detail previously [26–28]. In the present measurements, the spectrometer was operated at an incident electron energy of 1500 eV and a high energy resolution of about 65 meV. The background pressure in the interaction chamber was about $5 \times 10^{-5}$ Pa. Since the inelastic scattering intensities of the inner-shell excitations in N$_2$ are extremely low, a gas cell was used instead of a conventional nozzle to increase the density of nitrogen molecules in the collision region. In addition, a multichannel detection system enhanced the detection efficiency by about 20 times [28], which also facilitated the present experiment. It should be mentioned that the incident electron energy of 1500 eV might be not high enough for the validity of the first Born approximation (FBA) compared to the excitation energy of about 400 eV [29, 30]. However, the experiment was designed to determine the energy level structure of the inner-shell transitions in nitrogen molecule, rather than the absolute generalized oscillator strength. The invalidity of the FBA as well as the pressure effects [31] do not make any sense to the present experiment. The rotatable analyzer enables the measurements at several scattering angles between 1$^\circ$ and 8$^\circ$. The real zero angle was calibrated by the symmetry of the angular distribution of the inelastic scattering signals of $1s^2(1S_0) \rightarrow 1s2p(1P_1)$ transition of He around the geometry nominal 0$^\circ$.

To resolve the vibronic excitations at different momentum transfers, a least-squares fitting was used to fit the measured energy loss spectra. In the fitting, a Lorentzian function (natural line shape) was convoluted with a Voigt function (to approximate the instrumental response) to simulate the isolated transitions. The spectral profile of the $1s^2(1S_0) \rightarrow 1s2p(1P_1)$ transition of He can be well depicted by a Voigt function with an energy resolution of 65 meV. Thus, the instrumental function with a Voigt profile was adopted to fit the 1s excitation in N$_2$, while the energy resolution may be different considering the large energy difference between $1s^2(1S_0) \rightarrow 1s2p(1P_1)$ transition of He and the 1s excitation in N$_2$. The energy positions and natural widths of the Lorentzian for the vibronic excitations of the dipole-allowed transitions $1s\sigma_u \rightarrow 1\pi_g$ were fixed to the ones measured by Brion and Hitchcock [32]. This is reasonable since the measurements [32] were carried out under a similar condition, i.e., comparable incident electron energy and energy resolution, while at a small momentum transfer. To reduce the degree of freedom during the fitting, the intensity distribution measured at the synchrotron radiation [33] was adopted to fit the intensities of dipole-allowed transitions $1s\sigma_u \rightarrow 1\pi_g$. The Voigt profiles were shared for different vibronic transitions at the same scattering angle since the measured spectra covered only 3.5 eV. These assumptions were also addressed in reference [4] to fit the photoelectron spectra. The vibronic energies of a definite electronic state can be expressed as

$$E \approx E_{el} + \hbar \omega \left( \nu + \frac{1}{2} \right),$$

where $E_{el}$ is the electronic transition energy. $\hbar \omega$ is the vibrational energy with the angular frequency of $\omega$ which depends on the potential curve. $\nu$ is the vibrational quantum number. The energy splitting between the two components $\Delta E = E_{P \sigma_u}^{1\pi_g} - E_{P \sigma_g}^{1\pi_g}$ and the vibrational angular frequency between the two transitions $\Delta \omega = \omega^{1\nu_u} - \omega^{1\nu_g}$ were determined at the scattering angle of 1$^\circ$ and fixed for the spectra at larger scattering angles. The largest statistical counting at 1$^\circ$ yielded lowest fitting errors.

3. Results and discussion

As mentioned in the introduction, if the core-hole is delocalized, the experimental spectra should consist of two series of vibrational states ($1s\sigma_u \rightarrow 1\pi_g$ and $1s\sigma_g \rightarrow 1\pi_g$), due to the relaxation of the dipole selection rules for the collision experiment at large momentum transfers [25]. Otherwise, if the core-hole is localized, the measured spectra should only consist of one vibrational state ($1s \rightarrow 1\pi_g$). The measured spectra at the scattering angle of 1$^\circ$ and the fitted curves under the two assumptions are presented in figure 2. The first six vibrational states are resolved in the present measured spectra, which is consistent with the photoabsorption experiment [33]. To make a more intuitive comparison, the residuals of the fitted curves are also shown in figure 2. It is notable that the residuals of the fitted results with both series of vibrational states are less than
Figure 2. Electron energy loss spectrum of the inner-shell excitations of N₂ at scattering angle of 1° along with the fitted curves under the assumption of (A) delocalization and (B) localization. Lower panels (a) and (b) are the residuals for the fitted results of (A) and (B), respectively.

Table 1. The energy splitting between the two components

|                  | Energy splitting (meV) |
|------------------|------------------------|
| Present work     | 67 ± 7                 |
| Hergenhahn et al [4] | 97 ± 3                |
| Ehara et al [5]  | 100                    |
| Fukuzawa et al [6] | 80                    |
| Theoretical calculation |                  |
| Rescigno and Orel [34] | 70                    |
| Bielschowsky et al [35] | 60                    |

The residuals with only one series of vibrational states, which indicates that the assumption of delocalization can account for the observations better.

The energy splitting between the two components $\Delta E = E_{\Pi}^{g} - E_{\Pi}^{u}$ and the vibrational frequency difference $\Delta \hbar \omega$ are determined to be $67 \pm 7$ meV and $29 \pm 5$ meV, respectively. Previously, Ehara et al [5] calculated the potential energy curves of $1\sigma_{g}^{-1}$ and $1\sigma_{u}^{-1}$ ionized states of N₂ and their results showed that the potential energy curve of $1\sigma_{g}^{-1}$ is shallower than the one of $1\sigma_{u}^{-1}$. Therefore, the vibrational frequency of $1\sigma_{g}^{-1}$ should smaller than the one of $1\sigma_{u}^{-1}$, which agrees with present result. As shown in table 1, the resulted energy splitting agrees well with the theoretical predictions of 50–70 meV by the limited configuration-interaction [34] and generalized multistructural [35] wavefunctions. Although Rescigno and Orel [34] and Bielschowsky et al [35] calculated several results with different wave functions, the best results are listed in the table. The observed splitting in the photoionization [4–6] are larger than the present result due to the extra electron in the case of inner-shell excitation. However, the observed energy splitting indicates that the core-hole splits into two components of $(1\sigma_{g}^{-1})(1\pi_{g})^{1}$ and $(1\sigma_{u}^{-1})(1\pi_{g})^{1}$, i.e., the core-hole is delocalized over both nitrogen atoms in the excitation process.

Furthermore, it is well-known that the differential cross section (DCS) of a dipole-allowed transition usually decreases with $K^2$ increasing while the DCS of a dipole-forbidden transition increases at small $K^2$ and then decreases with $K^2$ increasing [29, 36]. Therefore, the intensity ratio between the dipole-forbidden $(1\sigma_{g})^{-1}(1\pi_{g})^{1}$ and dipole-allowed $(1\sigma_{u})^{-1}(1\pi_{g})^{1}$ transitions should feature as increasing with $K^2$ to reach
Figure 3. Electron energy loss spectra at the scattering angles (a) 2°, (b) 4°, and (c) 8° as well as (d) the transition intensity ratios between the $1\sigma_u^{-1}(1\pi_g)^1$ and $1\sigma_g^{-1}(1\pi_g)^1$ states.

4. Summary and conclusion

To summarize, both dipole-allowed $1\sigma_u^{-1}(1\pi_g)^1$ and dipole-forbidden $1\sigma_g^{-1}(1\pi_g)^1$ excitations of N$_2$ are observed at large momentum transfers. The measurement was performed by employing an angle-resolved EELS operated at an energy of 1500 eV and an energy resolution of 65 meV. The energy splitting between the $1\sigma_u^{-1}(1\pi_g)^1$ and $1\sigma_g^{-1}(1\pi_g)^1$ states is determined to be 67 ± 7 meV, according with the theoretical predictions of 60–70 meV. In addition, the transition intensity ratio between the $1\sigma_u^{-1}(1\pi_g)^1$ and $1\sigma_g^{-1}(1\pi_g)^1$ components features as typical behaviors of dipole-allowed and dipole-forbidden transitions, i.e., increasing to a maximum and then decreasing with the momentum transfer. Moreover, the derived relative Franck–Condon factor for the dipole-forbidden component is independent with the momentum transfer, which follows the Franck–Condon principle. All these observations for the behaviors of dipole-forbidden $1\sigma_g \rightarrow 1\pi_g$ transition suggest that there is indeed a dipole-forbidden component, i.e., the core-hole created by the inner-shell excitation is delocalized.
Figure 4. Relative Franck–Condon factor for the $^3\Pi_g (\nu = 0, 1, 2, 3)/^3\Pi_g$. The light gray shadows indicate an uncertainty of 10%.

It should be pointed out that only the electronic excitations are measured in the present study, which leads to the sum of symmetry-forbidden and symmetry-allowed component in the spectrum. The 'which way' information cannot be reflected and the symmetry is not broken by the measurement. The entire entangled state is not projected to the localized hole, and the core-hole state produced in the excitation process does not embody the localized core-hole state. The difference between the present work and the coincidence experimental results [18, 19] indicates that the different detection mechanisms lead to different phenomenon.

Acknowledgments

This work was jointly supported by the National Natural Science Foundation of China (Grants No. U1932207 and No. 12104437), the National Key Research and Development Program of China (Grant No. 2017YFA0402300) and the Fundamental Research Funds for the Central Universities. We thank the Heavy Ion Research Facility in Lanzhou (HIRFL) for their financial support.

Data availability statement

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

ORCID iDs

Shu-Xing Wang https://orcid.org/0000-0002-6305-3762
Lin-Fan Zhu https://orcid.org/0000-0002-5771-0471
References

[1] Kosugi N 2003 Chem. Phys. 289 117–34
[2] Bagus P S and Schaefer H F 1972 J. Chem. Phys. 56 224–6
[3] Cederbaum L S and Domcke W 1977 J. Chem. Phys. 66 5084–6
[4] Hergenhahn U, Kugeler O, Rüdel A, Rennie E E and Bradshaw A M 2001 J. Phys. Chem. A 105 5704–8
[5] Ehara M et al 2006 J. Chem. Phys. 124 124311
[6] Pütter R, Fukuzawa H, Liu X-J, Semenov S K, Cherepkov N A, Tanaka T, Hoshino M, Tanaka H and Ueda K 2008 J. Phys. B: At. Mol. Opt. Phys. 41 141001
[7] Sorensen S L, Miron C, Feifel R, Piancastelli M-N, Björneholm O and Svensson S 2008 Chem. Phys. Lett. 456 1–6
[8] Rolles D et al 2005 Nature 437 711–5
[9] Borse P J, Sarthore L J, Thomas T D, Carroll T X, Berrah N, Bozek J D and Kukla E 2000 Phys. Rev. A 63 012506
[10] Semenov S K et al 2005 J. Phys. B: At. Mol. Opt. Phys. 39 575–86
[11] Dill D, Wallace S, Siegel J and Dehmer J L 1978 Phys. Rev. Lett. 41 1230–3
[12] Björneholm O et al 2000 Phys. Rev. Lett. 84 2826–9
[13] Adachi J I, Hosaka K, Teramoto T, Yamazaki M, Watanabe N, Takahashi M and Yagishita A 2007 J. Phys. B: At. Mol. Phys. 40 107–35
[14] Kreidi K, Jahnke T, Weber T, Havermeier T, Grisenti R E, Liu X-J, Semenov S K, Tannaka T, Tanaka H and Ueda K 2008 J. Phys. B: At. Mol. Opt. Phys. 41 101002
[15] McCurdy C W, Rescigno T N, Trevisan C S, Lucchese R R, Gaire B and Menssen A 2017 Phys. Rev. A 95 011401
[16] Domcke W and Cederbaum L S 1977 Chem. Phys. 25 189–96
[17] Kivimäki A, Kemptens B, Maier K, Köppe H M, Piancastelli M N, Neib M and Bradshaw A M 1997 Phys. Rev. Lett. 79 998–1001
[18] Schöller M S et al 2008 Science 320 929–33
[19] Guillemin R, Declive P, Stener M, Bonme C, Marlin T, Journel L, Marchenko T and Kushwaha R 2014 Nat. Commun. 6 6166
[20] Ueda K 2008 Science 320 884–5
[21] Chen C T, Ma Y and Sette F 1989 Phys. Rev. A 40 6737–40
[22] Gadea F X, Köppel H, Schirmer J, Cederbaum L S, Randall K J, Bradshaw A M, Ma Y, Sette F and Chen C T 1991 Phys. Rev. Lett. 66 883–6
[23] King G C, Read F H and Tronc M 1977 Chem. Phys. Lett. 52 50–4
[24] Shaw D A, King G C, Read F H and Crejanovic D 1982 J. Phys. B: At. Mol. Phys. 15 1785–93
[25] Zhu L-F, Tian H-C, Liu Y-W, Kang X and Liu G-X 2015 Chin. Phys. B 24 043101
[26] Wu S L, Zhong Z P, Feng R F, Xing S L, Yang B X and Xu K Z 1995 Phys. Rev. A 51 4494
[27] Xu K Z, Feng R F, Wu S L, Ji Q, Zhang X J, Zhong Z P and Zheng Y 1996 Phys. Rev. A 53 3081–6
[28] Liu X-J, Zhu L-F, Jiang X-M, Yuan Z-S, Cai B, Chen X-J and Xu X-K 2001 Rev. Sci. Instrum. 72 3357–61
[29] Kang K et al 2019 J. Phys. B: At. Mol. Opt. Phys. 52 1–6
[30] Chen T, Liu Y-W, Xu Y-C and Zhu L-F 2020 J. Phys. B: At. Mol. Opt. Phys. 53 085201
[31] Zhong Z P, Feng R F, Xu K Z, Wu S L, Zhu L F, Zhang X J, Ji Q and Shi Q C 1997 Phys. Rev. A. 55 1799–809
[32] Hitchcock A P and Brion C E 1980 J. Electron Spectrosc. Relat. Phenom. 18 1–21
[33] Hergenhahn U, Kugeler O, Rüdel A, Rennie E E and Bradshaw A M 2001 J. Phys. Chem. A 105 5704–8
[34] Rescigno T N and Orel A E 1979 J. Chem. Phys. 70 3390–4
[35] Bielschowsky C E, Nascimento M A C and Hollauer E 1992 Phys. Rev. A 45 7942–7
[36] Liu Y-W, Xu L-Q, Ni D-D, Xu X, Huang X-C and Zhu L-F 2017 J. Geophys. Res: Space Physics 123 3459–68
[37] Trajmar S, Cartwright D C and Williams W 1971 Phys. Rev. A 4 1482–92
[38] Peng Y G et al 2014 Phys. Rev. A 89 032512