

Observation of a collective two-electron molecular resonance

J. Rist¹, M. Weller¹, M. Kircher¹, D. Trabert¹, N. Melzer¹, J. Siebert¹, I. Vela-Perez¹, M. Waitz¹, G. Kastirke¹, S. Eckart¹, S. Grundmann¹, M. S. Schöffler¹, R. Dörner¹, F. Trinter^{1,2,*} and T. Jahnke^{3,4,†}

¹*Institut für Kernphysik, Goethe-Universität Frankfurt, Max-von-Laue-Straße 1, 60438 Frankfurt am Main, Germany*

²*Molecular Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany*

³*European XFEL, Holzkoppel 4, 22869 Schenefeld, Germany*

⁴*Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany*



(Received 26 February 2023; revised 25 October 2023; accepted 15 November 2023; published 22 December 2023)

Unbound electrons can experience resonant scattering and transient trapping in a molecular potential. In molecular photoemission, these shape resonances manifest as peaks in the cross section with a width of several electron volts. They depend on the details of the molecular potential and the wavelength of the photoelectron. We report experimental results on photo double-ionization which show the phenomenon of a collective two-electron resonance which occurs when the de Broglie wavelength of the *dielectron* quasiparticle is similar to that of a single electron exhibiting a single-electron shape resonance.

DOI: [10.1103/PhysRevResearch.5.043283](https://doi.org/10.1103/PhysRevResearch.5.043283)

I. INTRODUCTION

A vital difference between atomic and molecular photoemission is the influence of the anisotropic molecular potential on the emitted electron. As the electron emerges from the molecule, it is (multiply) scattered by the molecular potential, which yields in some cases photoelectron waves in the continuum, that possess contributions from higher angular momenta as compared with corresponding atomic photoelectrons. For example, if a *K*-shell electron is emitted from a molecule, it will not only have *p*-wave character in the continuum, but in some cases show additional contributions from *d* and *f* waves [1,2]. This has interesting (and well studied) consequences. The additional angular momentum adds a centrifugal term to the molecular potential which finally manifests as an additional potential barrier the photoelectron has to overcome on its way out of the molecule. Depending on its wavelength, the photoelectron is even transiently trapped within this barrier, penetrating through it after some time via tunneling. This mechanism is at the heart of *shape resonances*, which occur typically close to the electron's ionization threshold in form of rather broad resonance features in the total photoionization cross section. The topic of shape resonance has been extensively studied in the past (see, e.g., Ref. [3] for a concise review). It is known that nitrogen molecules are prime candidates to observe shape resonances [4,5]. For example, in

K-shell ionization, a σ^* shape resonance appears as a broad feature at a photon energy of approximately $h\nu = 419$ eV [6–8]. This corresponds to a photoelectron energy of approximately 10 eV, i.e., the shape resonance occurs at an electron momentum of approximately 0.9 a.u. in the case of *K*-shell ionization. Similar findings have been reported for valence ionization [9,10]. For example, Hikosaka and Eland have shown that clear signatures of a σ shape resonance are visible at photon energies of $h\nu = 40.8$ eV and $h\nu = 48.8$ eV when forming the dissociative states $(2\sigma_g)^{-1} 2\Sigma_g^+$ and $F 2\Sigma_g^+$, respectively [11]. Just as in the *K*-shell case, at these photon energies, the emitted electron has a momentum close to one atomic unit. In the following, we briefly revisit the dissociative single-ionization case and then inspect the single-photon double ionization of N_2 .

II. EXPERIMENT

Our experiment was performed using cold target recoil ion momentum spectroscopy (COLTRIMS) [12–14]. Measurements were carried out at the UE112_PGM-1 beamline at the BESSY II electron storage ring operated by the Helmholtz-Zentrum Berlin für Materialien und Energie [15] running in single-bunch mode. In the experimental setup, the photon beam was intersected with a supersonic gas jet of N_2 molecules. Ions and electrons created in a photoreaction were guided by electric and magnetic fields to two time- and position-sensitive microchannel-plate detectors with delay-line position readout. The spectrometer consisted of a 182-mm-long electron arm incorporating Wiley-McLaren time-of-flight focusing [16] and an ion arm with a single acceleration region of 70 mm length. Large hexagonal delay-line detectors [17] with a diameter of 120 mm were employed for the ion and the electron measurement. A magnetic field of $B = 5.5$ Gauss was used to confine electrons up to a kinetic energy of 25 eV within the spectrometer volume.

*trinter@fhi-berlin.mpg.de

†till.jahnke@xfel.eu

Published by the American Physical Society under the terms of the [Creative Commons Attribution 4.0 International license](https://creativecommons.org/licenses/by/4.0/). Further distribution of this work must maintain attribution to the author(s) and the published article's title, journal citation, and DOI. Open access publication funded by the Max Planck Society.

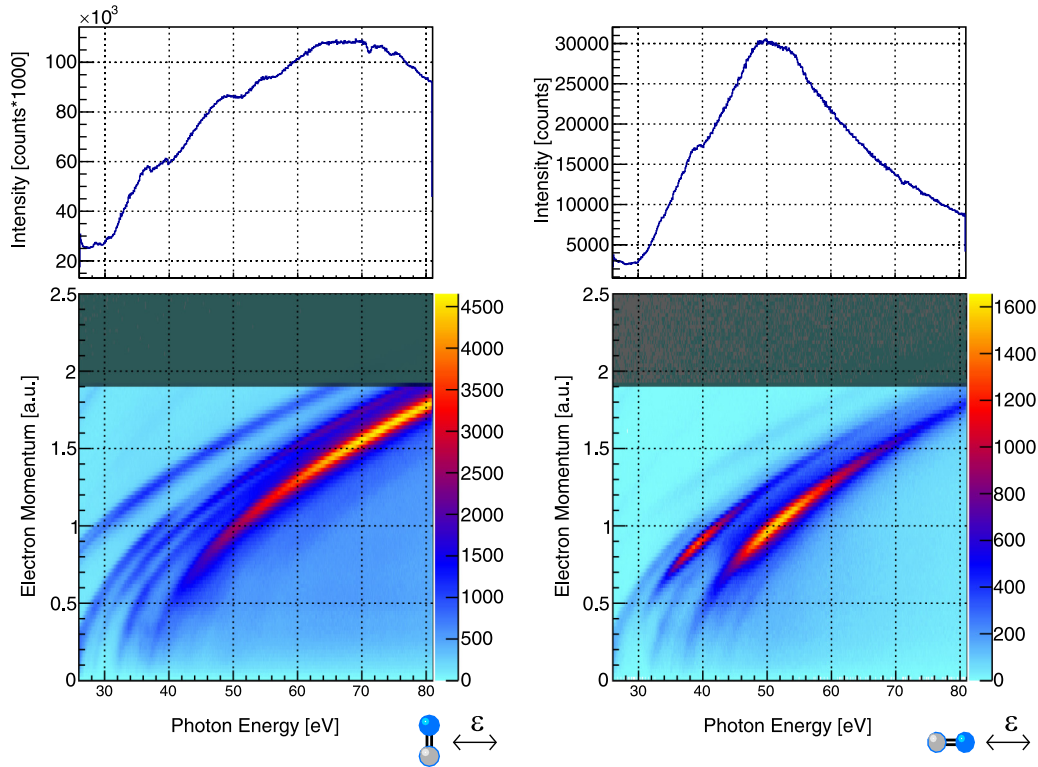


FIG. 1. (Top panel) Total ion yield for single ionization accompanied by dissociation into N^+ and N^0 . (Bottom panel) Correlation maps showing the dependence of the electron momentum on the photon energy. The left column shows the measured data for perpendicular orientation of the molecule with respect to the polarization axis of the ionizing light, the right column depicts the results for parallel orientation of the molecule. Note that the electron detection does not cover 4π solid angle for electrons above 1.8 a.u. momentum, the corresponding range is grayed out accordingly in the bottom panels.

The experimental study covered a photon-energy range of $h\nu = 28$ eV to $h\nu = 80$ eV scanning the photon energy in steps of 100 meV. All charged particles created by the photon interaction were detected in coincidence. By reconstructing their individual trajectories inside the COLTRIMS analyzer from their arrival times and the positions of impact on the detector, their initial vector momenta were deduced in an offline analysis. We obtained from the measured momenta in addition all deduced quantities, such as, for example, particle emission directions and kinetic energies. The measurement scheme allowed in particular to distinguish single from double (or even triple) ionization events and to determine whether the molecular ion dissociated in the final state or remained intact. The breakup direction of the dissociating molecules yielded the laboratory-frame orientation at the instant of the fragmentation and allowed to determine the orientation of the molecule with respect to the polarization direction of the ionizing synchrotron light.

III. RESULTS AND DISCUSSION

The detailed features of a shape resonance are determined by the exact molecular potential. The most sensitive ingredient to the energetic location of the resonance, however, is the photoelectron wavelength. An example is again photoionization of N_2 where the resonances for K -shell and valence electrons occur at very similar electron energies (if the N_2 molecule is oriented in parallel to the polarization vector of the ionizing light). To demonstrate this rather general con-

cept, we examine, just as Hikosaka and Eland, the breakup of the molecule into N^+ and N^0 after single ionization [11]. The measured electron momenta in dependence of the photon energy are depicted in Fig. 1 for this dissociation channel. The experimental results for the case of the molecule being oriented perpendicularly to the light's polarization vector are depicted in the left column, the corresponding data for parallel orientation in the right column. The latter shows a strong peak in the photon-energy-dependent ionization yield (top row) which is missing for perpendicular orientation. Note that the decrease in the ionization yield for perpendicular orientation of the molecule is an experimental artifact. The COLTRIMS analyzer is only covering full solid angle of detection for electrons with momenta up to 1.8 a.u., and as the momenta exceed this value at highest photon energies, the total detected ion yield diminishes as only full ion-electron coincidence events are considered here. The corresponding part of the histogram is grayed out in Fig. 1, bottom panels. The two-dimensional histograms depicting the measured electron momenta in dependence of the photon energy disclose the origin of the strong peak (and the small shoulder at a photon energy of approximately 40 eV) for parallel orientation of the molecule. The electron emission is enhanced if the electron momentum is in the range of 0.9 a.u., a trend which is clearly visible for the two strongest contributing final ionic states. These are at higher photon energies the $(2\sigma_g)^{-1} 2\Sigma_g^+$ state and at lower photon energies the $F 2\Sigma_g^+$ shakeup state resulting in the shoulder in the total ion yield. Inspecting the molecular-

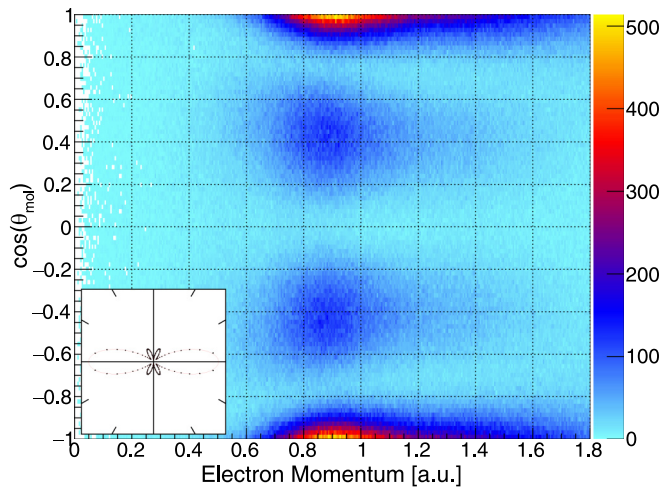


FIG. 2. Molecular-frame photoelectron angular distribution $\cos(\Theta_{\text{mol}})$ of the $(2\sigma_g)^{-1}2\Sigma_g^+$ state in dependence of the electron momentum. The molecule is oriented in parallel to the polarization direction of the light. The inset shows the angular distribution for an electron momentum $e_{\text{mom}} = 1$ a.u., i.e., on the shape resonance, the red line is a fit of a sum of Legendre polynomials up to $l = 9$ to the data. The angular distribution has been symmetrized.

frame photoelectron angular distribution for these two states at photon energies which correspond to their maximum contribution confirms that these broad resonance features can be attributed to a shape resonance. The angular distribution of the $(2\sigma_g)^{-1}2\Sigma_g^+$ state is depicted in Fig. 2 and shows the aforementioned f -wave (i.e., higher angular momentum) contributions, which have been observed and analyzed in previous work [11]. The inset in Fig. 2 depicts the molecular-frame angular distribution of the electron on top of the resonance.

In the literature, shape resonances are considered a single-electron effect. Resonances involving more than one electron are typically not attributed to this phenomenon, in particular, doubly excited states can yield resonance features which have been mistakenly interpreted as shape resonances in the past [3]. With respect to real photo double-ionization electron-emission effects, Wehlitz *et al.* reported in 2012 the observation of a resonance feature in the double ionization of benzene. They concluded that they observed a Cooper-pair-like emission with the emitted electron pair forming only due the geometrical properties of the benzene ring [18]. Follow-up studies by Jänkälä *et al.* confirmed the existence of the resonance feature in benzene (and its absence in pyrrole molecules, which consist, other than benzene, of a five-member ring), but contradicted the Cooper-pair interpretation [19]. They suggested that the observed feature is yet connected to the geometry of the molecule as a two-electron pendant to previously observed one-electron resonances. In the spirit of these findings, we inspect now the photo double-ionization of nitrogen molecules. Figure 3 shows an analogous representation of our measured data as the one in Fig. 1, with the difference being that now the results for photo double-ionization and a breakup of the molecule into N^+ and N^+ are shown. The molecule is oriented perpendicularly to the

polarization axis of the light in the left half of the figure, on the right half the results for parallel orientation are shown. As in the case of single ionization and dissociation, a broad peak structure can be seen in the total ion yield in case of a parallel orientation of the molecule, which is absent if the molecule is oriented perpendicularly. The middle row of the figure shows the dependence of the individual momentum of the two electrons on the photon energy, the bottom row depicts the corresponding dependence of the sum momentum of the two electrons. As the photon energy exceeding the binding energy can be shared between the two emitted electrons, the single-electron momenta are broadly distributed. However, from these figures it is obvious that the enhanced double-ionization yield of the molecule for σ orientation has a corresponding feature visible rather in the sum momentum of the two emitted electrons than in the single-electron momenta. Strikingly, the maximum of the peak observable in the sum-momentum panel on the right is located at a momentum of $p_{\text{sum}} = 1$ a.u., i.e., at a similar value as in the case of dissociative single ionization (and the aforementioned K -shell ionization as well). We therefore argue that we have observed a resonance feature which is similar to the well-known one-electron shape resonances. However, this “shape resonance” appears in the double-ionization continuum and its location is not connected to the momentum (i.e., wavelength) of the two individual electrons. It appears that the de Broglie wavelength of the two-electron quasiparticle, i.e., the *dielectron*, is similar to that of a single electron experiencing a single-electron shape resonance. It should be noted that comparing the sum-momentum distribution in Fig. 3 with the momentum distributions shown in Fig. 3, the sum momenta seem surprisingly broad. The width of this distribution can be attributed to the fact that not a single (repulsive) dissociative state of the N_2^{2+} molecular ions is populated as the photon energy is scanned. There is a manifold of such states with a steeply repulsive slope in the Franck-Condon region [20] that can be populated by the double-photoionization process. Accordingly, as several repulsive states contribute at different energies, the sum-momentum distribution is expected to be comparably broad. In addition, the observed resonance feature is broader (in photon energy) as compared with those shown in Fig. 1. This can be attributed to the just-mentioned manifold of doubly ionized states, as well. Furthermore, the exact shape of a traditional shape resonance depends on delicate details of the potential of the molecular ion. For example, the width of the resonance differs already strongly for the vibrational ground state of the ion as compared with its vibrationally excited states [21]. In the present case of observing a resonance feature in the double-ionization continuum, we therefore do not expect it to directly mimic the shape or width of the single-valence-ionization resonance.

This perspective of a dielectron quasiparticle whose momentum vector dictates the characteristics of double ionization has been shown to be fruitful already in double-ionization studies of H_2 . There it has been shown that it is the sum momentum of the dielectron which shows two-center interferences [22,23] while the individual electrons have rather featureless angular distributions [24,25]. Along the same lines, selection rules also have been expressed successfully

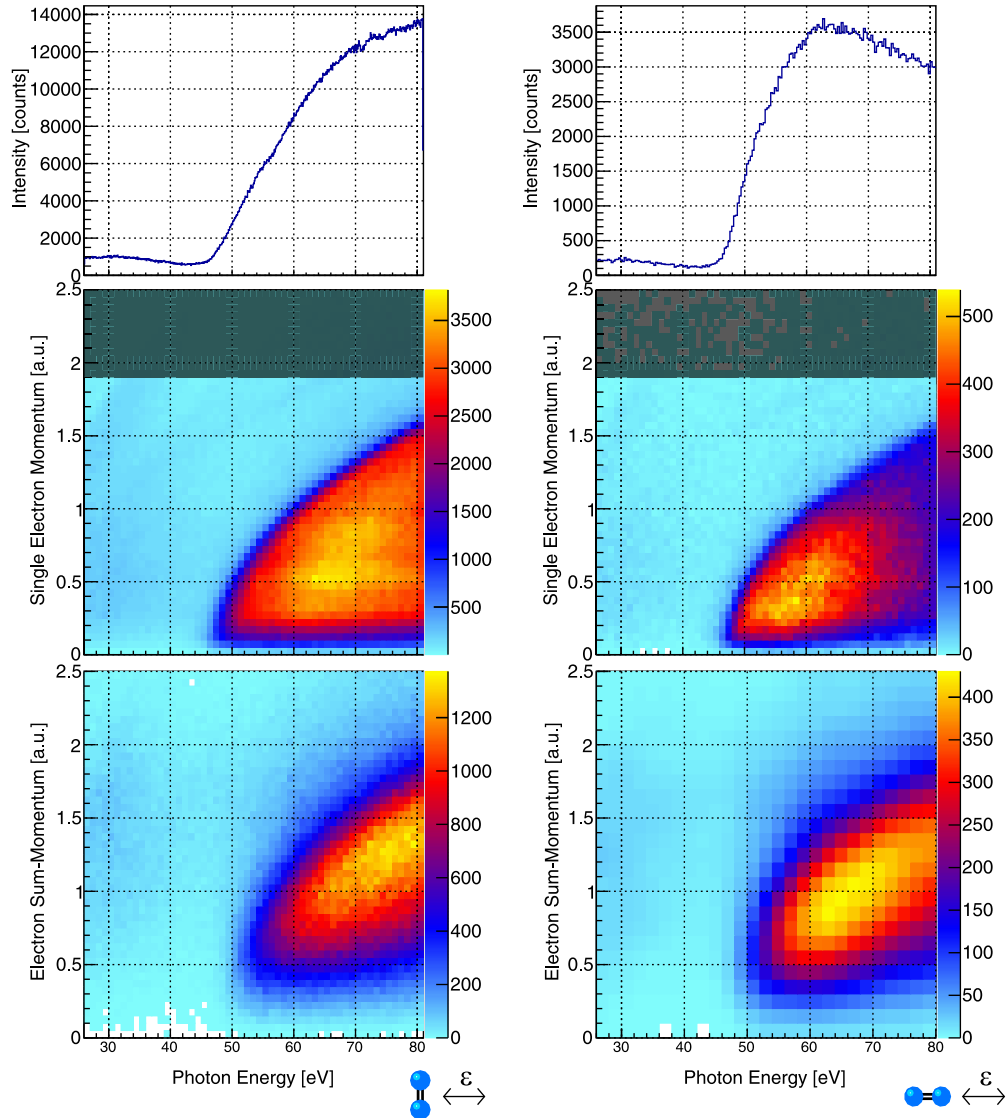


FIG. 3. Results for photo double-ionization of N_2 leading to a breakup into N^+ and N^+ . (Left panel) The molecule is oriented perpendicularly to the polarization vector of the ionizing light. (Right panel) Results for parallel orientation of the molecule. The top row shows the photon-energy-dependent ion yield, the middle row depicts the momentum of one of the two emitted electrons, and the bottom row the sum momentum of the two electrons.

in terms of the momentum of the dielectron in the past [26]. We have to admit, however, that the molecular-frame angular distribution of the two-electron quasiparticle is less clearly pronounced with respect to the expected f -wave features in the present case. The corresponding angular distribution is shown in Fig. 4. As outlined before, a manifold of doubly charged final states exist which are responsible for the broad sum-momentum distributions in Fig. 3. As each of these final states has a different binding energy, the resulting electron sum energy depends on the populated final state. Therefore, if we integrated over all these states, several different *dielectron* wavelengths would contribute. To reach a case where the sum energy of the two electrons is fixed, we restricted the dataset shown in Fig. 4 to a small range of photon energies on top of the resonance, i.e., to $64 \text{ eV} < h\nu < 66 \text{ eV}$. In addition, we chose from the remaining dataset those cases where the total sum energy of all measured particles is

$KER + E_{e1} + E_{e2} = 40 \text{ eV} \pm 1.5 \text{ eV}$ and selected electrons with a sum momentum to a range of $0.6 \text{ a.u.} < p_{\text{sum}} < 1.4 \text{ a.u.}$, i.e., at the maximum of the resonance visible in Fig. 3 for the σ orientation. The f -wave contributions might be less pronounced in Fig. 4 due to integrating over the extent of the ranges described above, which is equivalent to integrating over a range of electron wavelengths. Furthermore, the resonant contribution to the photon-energy-dependent yield seems smaller for the doubly ionized case as compared with single ionization, which might yield a less clear f -wave contribution as well. Finally, in previous studies, a blurring of the angular distribution was found in CO molecules in cases where the axial-recoil approximation failed [27]. Given the properties of the direct double-ionization process as such, it is, however, less probable that the latter effect is the underlying cause for the loss of angular features in the present case.

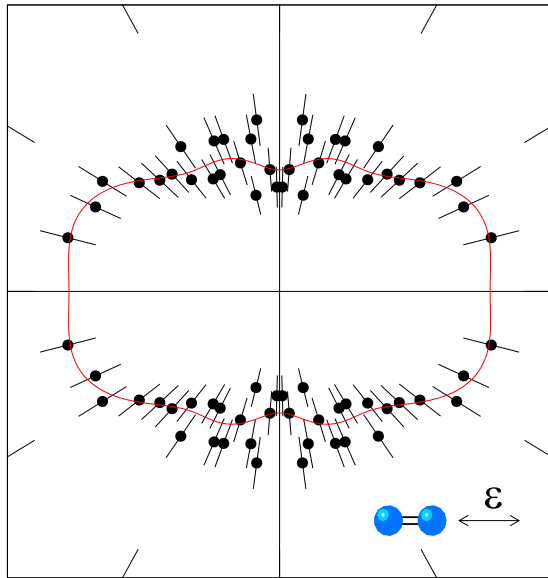


FIG. 4. Molecular-frame angular distribution of the two-electron quasiparticle on top of the σ resonance visible in Fig. 3, left. The molecule is oriented in parallel to the polarization axis of the ionizing photons. The line is a fit of a sum of Legendre polynomials up to $l = 9$ to the data.

IV. CONCLUSIONS

In conclusion, we examined the photoionization of nitrogen molecules using a COLTRIMS reaction microscope in a range of photon energies where several well-known shape resonances occur. We found a corresponding resonance feature in the photo double-ionization of the molecule, which is present only if the molecule is oriented parallel to the polarization direction of the ionizing light. We suggest that this resonance is a two-electron pendant to the well-known one-electron σ shape resonances. The broad resonance appears in a range of photon energies, where the sum momentum of the two emitted electrons is similar to that of single electrons experiencing a one-electron shape resonance, i.e., it appears in cases where the de Broglie wavelength of the *dielectron* is suitable for creating a shape resonance. While we report in this paper on our experimental findings, a full theoretical modeling of the two-electron emission process from the molecule would be favorable. We hope that our present work stimulates corresponding calculations.

ACKNOWLEDGMENTS

We thank Helmholtz-Zentrum Berlin (HZB) for the allocation of synchrotron radiation beam time. We would like to thank the staff at BESSY II for the excellent support during the beam time, in particular G. Schiwietz. This work was supported by Deutsche Forschungsgemeinschaft (DFG) and Bundesministerium für Bildung und Forschung (BMBF).

- [1] J. L. Dehmer and D. Dill, Shape resonances in K -shell photoionization of diatomic molecules, *Phys. Rev. Lett.* **35**, 213 (1975).
- [2] N. A. Cherepkov, G. Raseev, J. Adachi, Y. Hikosaka, K. Ito, S. Motoki, M. Sano, K. Soejima, and A. Yagishita, K -shell photoionization of CO: II. Determination of dipole matrix elements and phase differences, *J. Phys. B: At., Mol. Opt. Phys.* **33**, 4213 (2000).
- [3] M. N. Piancastelli, The neverending story of shape resonances, *J. Electron Spectrosc. Relat. Phenom.* **100**, 167 (1999).
- [4] J. B. West, A. C. Parr, B. E. Cole, D. L. Ederer, R. Stockbauer, and J. L. Dehmer, Shape-resonance-induced non-Franck-Condon vibrational intensities in $3\sigma_g$ photoionisation of N_2 , *J. Phys. B: At. Mol. Phys.* **13**, L105 (1980).
- [5] S. H. Southworth, A. C. Parr, J. E. Hardis, and J. L. Dehmer, Channel coupling and shape resonance effects in the photoelectron angular distributions of the $3\sigma_g^{-1}$ and $2\sigma_u^{-1}$ channels of N_2 , *Phys. Rev. A* **33**, 1020 (1986).
- [6] E. Shigemasa, J. Adachi, M. Oura, and A. Yagishita, Angular distributions of $1s\sigma$ photoelectrons from fixed-in-space N_2 molecules, *Phys. Rev. Lett.* **74**, 359 (1995).
- [7] B. Kempgens, A. Kivimäki, M. Neeb, H. M. Köppe, A. M. Bradshaw, and J. Feldhaus, A high-resolution N $1s$ photoionization study of the N_2 molecule in the near-threshold region, *J. Phys. B: At., Mol. Opt. Phys.* **29**, 5389 (1996).
- [8] U. Hergenhahn, O. Kugeler, A. Rüdell, E. E. Rennie, and A. M. Bradshaw, Symmetry-selective observation of the N $1s$ shape resonance in N_2 , *J. Phys. Chem. A* **105**, 5704 (2001).
- [9] S. Motoki, J. Adachi, K. Ito, K. Ishii, K. Soejima, A. Yagishita, S. K. Semenov, and N. A. Cherepkov, Direct probe of the shape resonance mechanism in $2\sigma_g$ -shell photoionization of the N_2 molecule, *Phys. Rev. Lett.* **88**, 063003 (2002).
- [10] S. Motoki, J. Adachi, K. Ito, K. Ishii, K. Soejima, A. Yagishita, S. K. Semenov, and N. A. Cherepkov, Complete photoionization experiment in the region of the $2\sigma_g \rightarrow \sigma_u$ shape resonance of the N_2 molecule, *J. Phys. B: At., Mol. Opt. Phys.* **35**, 3801 (2002).
- [11] Y. Hikosaka and J. H. D. Eland, Molecular-frame photoelectron angular distributions in inner-valence photoionization of N_2 , *J. Phys. B: At., Mol. Opt. Phys.* **33**, 3137 (2000).
- [12] R. Dörner, V. Mergel, O. Jagutzki, L. Spielberger, J. Ullrich, R. Moshhammer, and H. Schmidt-Böcking, Cold target recoil ion momentum spectroscopy: a ‘momentum microscope’ to view atomic collision dynamics, *Phys. Rep.* **330**, 95 (2000).
- [13] J. Ullrich, R. Moshhammer, A. Dorn, R. Dörner, L. Ph. H. Schmidt, and H. Schmidt-Böcking, Recoil-ion and electron momentum spectroscopy: reaction-microscopes, *Rep. Prog. Phys.* **66**, 1463 (2003).
- [14] T. Jahnke, Th. Weber, T. Osipov, A. L. Landers, O. Jagutzki, L. Ph. H. Schmidt, C. L. Cocke, M. H. Prior, H. Schmidt-Böcking, and R. Dörner, Multicoincidence studies of photo and Auger electrons from fixed-in-space molecules using the COLTRIMS technique, *J. Electron Spectrosc. Relat. Phenom.* **141**, 229 (2004).

- [15] G. Schiwietz, M. Beye, and T. Kachel, UE112_PGM-1: An open-port low-energy beamline at the BESSY II undulator UE112, *JLSRF* **1**, A33 (2015).
- [16] W. C. Wiley and I. H. McLaren, Time-of-flight mass spectrometer with improved resolution, *Rev. Sci. Instrum.* **26**, 1150 (1955).
- [17] O. Jagutzki, V. Mergel, K. Ullmann-Pfleger, L. Spielberger, U. Spillmann, R. Dörner, and H. Schmidt-Böcking, A broad-application microchannel-plate detector system for advanced particle or photon detection tasks: large area imaging, precise multi-hit timing information and high detection rate, *Nucl. Instrum. Methods Phys. Res., Sect. A* **477**, 244 (2002).
- [18] R. Wehlitz, P. N. Juranić, K. Collins, B. Reilly, E. Makoutz, T. Hartman, N. Appathurai, and S. B. Whitfield, Photoemission of Cooper pairs from aromatic hydrocarbons, *Phys. Rev. Lett.* **109**, 193001 (2012).
- [19] K. Jänkälä, P. Lablanquie, F. Penent, J. Palaudoux, L. Andric, and M. Huttula, Double photoionization in ring molecules: Search of the Cooper pair formation, *Phys. Rev. Lett.* **112**, 143005 (2014).
- [20] R. W. Wetmore and R. K. Boyd, Theoretical investigation of the dication of molecular nitrogen, *J. Phys. Chem.* **90**, 5540 (1986).
- [21] K. J. Randall, A. L. D. Kilcoyne, H. M. Köppe, J. Feldhaus, A. M. Bradshaw, J.-E. Rubensson, W. Eberhardt, Z. Xu, P. D. Johnson, and Y. Ma, Photon energy dependence of the high resolution C 1s photoelectron spectrum of CO in the threshold region, *Phys. Rev. Lett.* **71**, 1156 (1993).
- [22] H. D. Cohen and U. Fano, Interference in the photo-ionization of molecules, *Phys. Rev.* **150**, 30 (1966).
- [23] M. Waitz, D. Metz, J. Lower, C. Schober, M. Keiling, M. Pitzer, K. Mertens, M. Martins, J. Viehhaus, S. Klumpp, T. Weber, H. Schmidt-Böcking, L. Ph. H. Schmidt, F. Morales, S. Miyabe, T. N. Rescigno, C. W. McCurdy, F. Martín, J. B. Williams, M. S. Schöffler, T. Jahnke, and R. Dörner, Two-particle interference of electron pairs on a molecular level, *Phys. Rev. Lett.* **117**, 083002 (2016).
- [24] D. Akoury, K. Kreidi, T. Jahnke, Th. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. Ph. H. Schmidt, A. Czasch, O. Jagutzki, R. A. Costa Fraga, R. E. Grisenti, R. Díez Muiño, N. A. Cherepkov, S. K. Semenov, P. Ranitovic, C. L. Cocke, T. Osipov, H. Adaniya, J. C. Thompson, M. H. Prior, A. Belkacem, A. L. Landers, H. Schmidt-Böcking, and R. Dörner, The simplest double slit: Interference and entanglement in double photoionization of H₂, *Science* **318**, 949 (2007).
- [25] K. Kreidi, D. Akoury, T. Jahnke, Th. Weber, A. Staudte, M. Schöffler, N. Neumann, J. Titze, L. Ph. H. Schmidt, A. Czasch, O. Jagutzki, R. A. Costa Fraga, R. E. Grisenti, M. Smolarski, P. Ranitovic, C. L. Cocke, T. Osipov, H. Adaniya, J. C. Thompson, M. H. Prior, A. Belkacem, A. L. Landers, H. Schmidt-Böcking, and R. Dörner, Interference in the collective electron momentum in double photoionization of H₂, *Phys. Rev. Lett.* **100**, 133005 (2008).
- [26] T. J. Reddish and J. M. Feagin, Photo double ionization of molecular deuterium, *J. Phys. B: At., Mol. Opt. Phys.* **32**, 2473 (1999).
- [27] Th. Weber, O. Jagutzki, M. Hattass, A. Staudte, A. Nauert, L. Schmidt, M. H. Prior, A. L. Landers, A. Bräuning-Demian, H. Bräuning, C. L. Cocke, T. Osipov, I. Ali, R. Díez Muiño, D. Rolles, F. J. García de Abajo, C. S. Fadley, M. A. Van Hove, A. Cassimi, H. Schmidt-Böcking, and R. Dörner, *K*-shell photoionization of CO and H₂: is there a link between the photoelectron angular distribution and the molecular decay dynamics? *J. Phys. B: At., Mol. Opt. Phys.* **34**, 3669 (2001).