

Imaging SF₆ with *K*-shell molecular-frame photoelectron angular distributions

O. Dennis McGinnis^{1,*}, Nico Diehl², Laura Sommerlad¹, Andreas Pier¹, Niklas Melzer¹, Sven Grundmann¹, Nikolay M. Novikovskiy², Reinhard Dörner¹, Till Jahnke³, Florian Trinter^{4,†} and Philipp V. Demekhin^{2,‡}

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

²*Institut für Physik und CINSaT, Universität Kassel, Heinrich-Plett-Strasse 40, 34132 Kassel, Germany*

³*Max-Planck-Institut für Kernphysik, Saupfercheckweg 1, 69117 Heidelberg, Germany*

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



(Received 9 March 2026; accepted 8 May 2026; published 21 May 2026)

We report a joint experimental and theoretical study of *K*-shell photoionization of S and F atoms in sulfur hexafluoride, SF₆. In our experiment, we employed tunable synchrotron radiation to generate photoelectrons emitted from the 1s shells of the S and F atoms with different kinetic energies. Coincident electron- and fragment-ion detection, carried out using cold target recoil-ion momentum spectroscopy, enabled access to polarization-averaged molecular-frame photoelectron angular distributions. In addition, we performed electronic structure calculations within the relaxed-core Hartree-Fock approximation by using a stationary single-center method. The calculations are in good agreement with the experiment. Our results support previous findings on the feasibility of imaging three-dimensional atomic arrangements in molecules using polarization-averaged molecular-frame angular distributions. In particular, we demonstrate that such imaging is possible even at intermediate photoelectron kinetic energies and even for six experimentally undistinguished F 1s emitters.

DOI: [10.1103/68bc-m3y9](https://doi.org/10.1103/68bc-m3y9)

I. INTRODUCTION

Molecular-frame photoelectron angular distributions (MF-PADs [1–6]) are known to be very sensitive probes of molecular structure and dynamics (see also Ref. [7] for a recent review). In contrast to laboratory-frame angular distributions, MFPADs are mainly determined by the instantaneous spatial arrangement of the constituent atoms, which influences an outgoing photoelectron wave. The resulting distributions are thus given by a coherent superposition of multiple-scattered photoelectron waves, providing detailed information on the molecular geometry and the ionization process. Such multiple-scattering processes are particularly pronounced in the regime of lower photoelectron energies, i.e., below 15 eV, resulting in nonintuitive emission distributions of high complexity. In contrast, MFPADs of high-energy photoelectrons (e.g., higher than 70 eV) are more intuitive [8–10] and can be understood within the concept of electron diffraction imaging. In particular, they exhibit interference patterns that can already be explained within a single-scattering approximation and related to the distance between the emitter and scatterer atoms [11–13]. Moreover, the emission probabilities exhibit

prominent forward-scattering lobes pointing toward heavy neighbors [11–13], as if the photoelectron wave were focused by the nuclei. As can be shown theoretically [14,15], these features of the high-energy MFPADs survive averaging over all polarizations of the ionizing light and are also present in the polarization-averaged molecular-frame photoelectron angular distributions (PA-MFPADs).

Motivated by preceding experimental results on PA-MFPADs of low-energy photoelectrons in CH₄ [3,4], a theoretical work [16] performed a comprehensive study of *K*-shell ionization of small diatomic and polyatomic molecules over a very broad range of photoelectron kinetic energies. The authors of Ref. [16] found that, in cases where the addressed emitter atom has heavy neighboring atoms, the computed PA-MFPADs exhibit the aforementioned enhancement of the emission probability toward the neighbors even at selected intermediate photoelectron kinetic energies (see the Supplemental Material of Ref. [16] for an animated evolution of the computed distributions as functions of photon energy). When such an enhancement occurs, the respective PA-MFPADs thus encode structural information about the three-dimensional spatial arrangement of heavy atoms in the molecule. Among the molecules considered in Ref. [16], sulfur hexafluoride (SF₆) possesses high (octahedral) symmetry and a well-defined geometry. It contains only heavy atoms as neighbors to any possible emitter, which may enable imaging of its structure using PA-MFPADs at intermediate photoelectron kinetic energies. This assumption seems to be reasonable, since such photoelectrons, for which multiple-scattering effects are still pronounced, may also enable diffraction imaging (i.e., they share advantages of both low- and high-energy domains). In order to check the validity of this assumption,

*Contact author: mcginnis@atom.uni-frankfurt.de

†Contact author: trinter@fhi-berlin.mpg.de

‡Contact author: demekhin@physik.uni-kassel.de

we examine here the PA-MFPADs of SF_6 for the S $1s$ and F $1s$ shells at intermediate photoelectron kinetic energies of 28 and 38 eV, both experimentally and theoretically. The experimental and theoretical approaches are outlined in Secs. II and III, respectively. The obtained results are compared and discussed in Sec. IV. We conclude in Sec. V with a brief summary.

II. EXPERIMENT

The experiments were carried out at the soft X-ray beamline P04 [17] of the synchrotron PETRA III (DESY, Hamburg, Germany) in the few-bunch timing mode (bunch spacing 192 ns), using circularly polarized photons with nominal (not calibrated; see below) energies of about 725 eV (for F $1s$), 2515 eV, and 2525 eV (for S $1s$), generated by its APPLE II undulator. The SF_6 molecules were provided in a supersonic gas jet, which passed through two skimmers (300 m in diameter each) and was crossed with the photon beam at right angles. The gas nozzle had a diameter of 30 μm , and the driving pressure was 6.2 bar. For detection, we used the permanently installed cold target recoil-ion momentum spectroscopy (COLTRIMS) reaction microscope [18–20].

The spectrometer comprised an ion arm with an acceleration length of 16.7 cm and an electron arm with an acceleration length of 12.0 cm for the first set of measurements performed at the two photon energies of 725 and 2515 eV, while for the second campaign consisting of measurements at the energy of 2525 eV, it comprised an ion arm with an acceleration length of 13 cm and an electron arm with an acceleration length of 7 cm and a drift length of 12 cm. Both arms were equipped with microchannel plate detectors (active area 80 mm diameter) with hexagonal delay-line position readout [21]. Electrons and ions were guided by homogeneous electric fields of 42.8 V/cm (first campaign) and 49.4 V/cm (second campaign) and magnetic fields of 12.8 and 11.16 G, respectively, onto the time- and position-sensitive detectors. The field strengths were chosen to achieve a 4π collection solid angle for electrons with kinetic energies up to 57 and 43 eV in the two sets of measurements. Similarly, cases of two F^+ fragment ions emitted from the molecule at a relative angle of 90° were recorded for ion energies up to 7.5 and 13 eV, respectively. Since the nominal photon energies may deviate from the exact values by a few eV, we calibrated the electron kinetic energies of the spectrometer using N $1s$ photoelectrons from N_2 with well-known MFPADs [2].

Ionic fragments and photoelectrons were detected in coincidence. From the measured times of flight and impact positions, the three-dimensional momentum vectors of all charged fragments were reconstructed, along with derived quantities such as kinetic energies and emission angles. The momenta of the ionic fragments provide information on the orientation of the molecule in the laboratory frame of reference. This is possible if the molecule breaks up rapidly after ionization, so that it does not rotate significantly [22,23] (i.e., the axial recoil approximation [24] is satisfied). The recorded angular emission distribution of the two F^+ fragments, as a function of their relative emission angle, exhibits two sharp maxima: one centered at 90° and another at 180° , representing either two neighboring or two opposite fluorine atoms in SF_6 ,

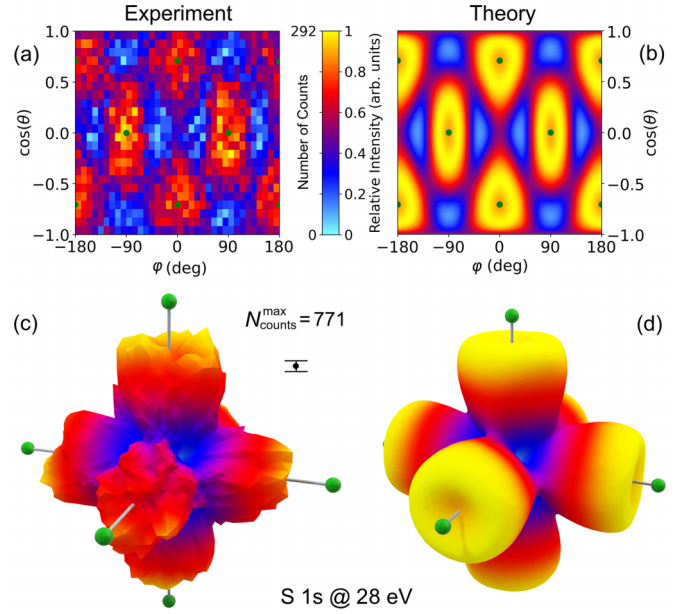


FIG. 1. (a), (c) Experimental and (b), (d) theoretical PA-MFPADs for S $1s$ photoelectrons emitted with a kinetic energy of 28 eV. (a), (b) Two-dimensional emission probability as a function of the polar and azimuthal electron emission angles, encoded in a color map. The theoretical distributions are normalized to their maxima and shown on relative scales. The sulfur atom is located at the origin, while the positions of the six fluorine atoms are shown in this molecular frame of reference by green dots. (c), (d) Three-dimensional representations of (a) and (b), where the emission probability is encoded in the distance from the origin using the same color-coded scale. The molecular orientation in space is indicated by the positions of the fluorine atoms (green balls). The number of counts $N_{\text{counts}}^{\text{max}}$, corresponding to the maximum of the experimental distribution, is listed on its right-hand side together with the maximal statistical uncertainty, given by $\sqrt{N_{\text{counts}}^{\text{max}}}$ and visualized by the black error bar. For better comparison, the theoretical data are additionally smoothed with a resolution of 10° in both angles.

respectively. Gating the coincident data on the former peak selects the fluorine atoms of two perpendicular molecular bonds. The kinetic energy release spectrum of two perpendicularly emitted F^+ fragments is sharp and structureless, indicating that the fragments are emitted with nearly equal energies and containing no clear information on the apparent localization of the F ($1s^{-1}$) holes [25] in the decay of SF_6 . In line with the molecular symmetry, we chose these two to define the xz plane, which contains four F atoms, while two remaining F atoms lie along the y axis, perpendicular to this plane. We then transformed the electron momentum vectors into this recoil frame to construct the MFPADs. As we did not restrict the data to specific molecular orientation with respect to the propagation direction of the circularly polarized synchrotron light, we obtained the PA-MFPADs reported in Figs. 1–3 below.

III. THEORY

We carried out our calculations of S $1s$ and F $1s$ photoionization of the SF_6 molecule using the stationary single-center method [26–29]. Similar to our very recent

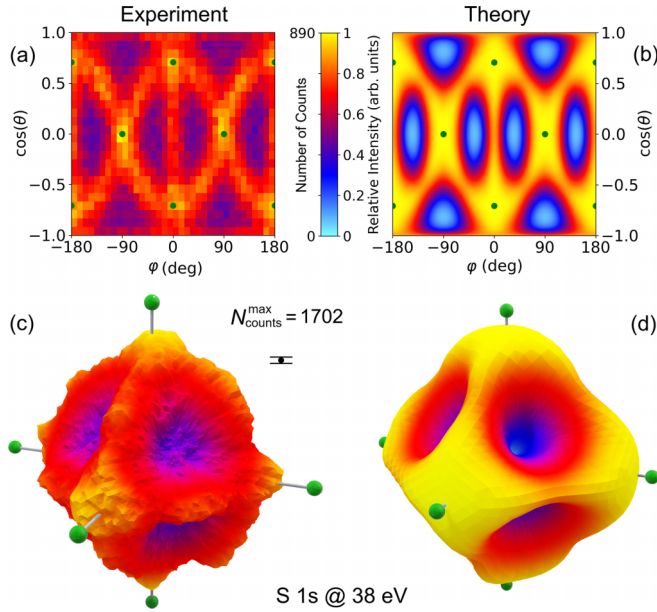


FIG. 2. The same as in Fig. 1, but for S 1s photoelectrons emitted with a kinetic energy of 38 eV. See the caption of Fig. 1 for details on the data representation.

works on inner-shell ionization of fenchone [30,31], we used the fixed equilibrium geometry of SF₆ [32] and employed the relaxed-core Hartree-Fock approximation. Briefly, the occupied molecular orbitals were generated with the PC GAMESS (US) [33] quantum-chemistry package using a triple zeta valence basis [34], augmented by two additional p and one d polarization functions. We accounted for the monopole relaxation of the bound orbitals of the ion caused by the created

core vacancy. This effect was simulated within the equivalent-core approximation using a fractional nuclear charge for the core-ionized atom [35,36]. For this purpose, when generating bound orbitals of the ion, the nuclear charge of the emitting atom in the molecule with all 70 electrons was increased by +0.5, modeling core relaxation on half of the created core vacancy. These bound orbitals were further represented by single-center expansions with $\ell \leq 99$ and employed to generate ionic potentials of the singly charged core-ionized molecule. These ionic potentials were then used to obtain the partial photoelectron continuum waves with $\ell \leq 29$ and subsequently to calculate dipole amplitudes for the electron transition from the chosen core orbitals of the neutral molecule into the continuum. The PA-MFPADs were obtained via explicit analytic equations derived in Ref. [37] and, in the case of F 1s ionization, additionally averaged over contributions from six equivalent localized emitters, computed via separate noncoupled-channel calculations [38].

IV. RESULTS AND DISCUSSION

The results of our study of S 1s ionization are depicted in Figs. 1 and 2, respectively, for photoelectron kinetic energies of 28 and 38 eV, while those of F 1s ionization at a kinetic energy of 28 eV are shown in Fig. 3. In each figure, the experimental PA-MFPADs are shown in the left-hand panels, while the theoretical ones are shown in the right-hand panels. The upper panels depict the two-dimensional emission probability via a color-coded map as a function of the electron emission angles θ and φ in the molecular frame of reference. The positions of the F atoms in this frame are indicated by green dots. In particular, as discussed in Sec. II, two F atoms appear on the y axis at $(\theta = 90^\circ, \varphi = \pm 90^\circ)$. For a better representation (such that none of the remaining F atoms appear on the z axis, where the azimuthal angle φ is not defined), we chose the positive direction of the molecular z axis along the sum of the momenta of the two F⁺ fragments, which were emitted under a relative angle close to 90° . Thereby, the respective green dots emerge at $(\theta = 45^\circ \text{ or } 135^\circ, \varphi = 0^\circ)$ and $(\theta = 45^\circ \text{ or } 135^\circ, \varphi = \pm 180^\circ)$, with all detected pairs of neighboring F⁺ ions being assigned to the same pair of green dots at $(\theta = 45^\circ, \varphi = 0^\circ \text{ or } \pm 180^\circ)$. These PA-MFPADs are shown again in the lower panels as three-dimensional distributions (see the figure captions for details), with the positions of the F atoms indicated by green balls on sticks. The Supplemental Material [39] offers an interactive view of these PA-MFPADs, where the three-dimensional distributions can be rotated and viewed from different directions.

Figures 1 and 2 demonstrate good agreement between the measured and computed PA-MFPADs of S 1s photoelectrons with kinetic energies of 28 and 38 eV. In contrast, the present distributions differ from the theoretical predictions of Ref. [16], which are available in the Supplemental Material of that publication as animated movies over a very broad photon-energy range. However, the present results agree well with their predictions made at (about 10 eV) lower kinetic energies, in particular at about 18 and 28 eV, respectively (corresponding to photon energies of about 2508 and 2518 eV). Note that, as indicated in the description of the movie, a binding energy of 2490 eV must be used to relate their photon

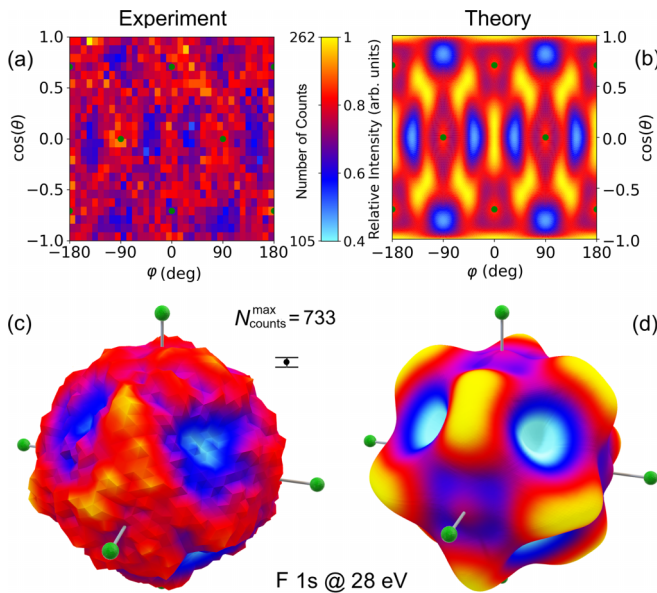


FIG. 3. The same as in Fig. 1, but for F 1s photoelectrons emitted with a kinetic energy of 28 eV. The theoretical distributions were averaged over the six fluorine atoms with equal weights. See the caption of Fig. 1 for details on the data representation. Note the different color scale used in this case.

and electron energy scales. This discrepancy might be caused by an insufficient accounting for core relaxation, which has a strong effect for such a deep inner-shell vacancy.

For 28 eV (Fig. 1), the distributions exhibit prominent lobes pointing from the emitter (the S atom located at the origin) toward all six scatterers (the F atoms), thereby reflecting the three-dimensional structure of SF₆. For the somewhat larger kinetic energy of 38 eV (Fig. 2), the photoemission distributions exhibit a rather different structure, without prominent lobes toward the F atoms. Nevertheless, even if the assignments of the emission direction of the F atoms to distinct features in the PA-MFPAD were not known, the three-dimensional structure of SF₆ could still be deduced from these distributions. For this purpose, one can exploit the molecular symmetry and search for a sixfold pattern in the distributions, as indicated by the green dots in Figs. 2(a) and 2(b) (note that the $\varphi = \pm 180^\circ$ sides of the two-dimensional representations correspond to the negative x axis and are equivalent). As can be seen, all other structures in the distributions are either eightfold (the dips) or 12-fold (the edges) and therefore cannot be related to the six F atoms.

Our computed and measured PA-MFPADs for the six indistinguishable F atoms acting as photoelectron emitters at a kinetic energy of 28 eV are shown in Fig. 3. Because of averaging over six contributions, the respective distributions exhibit less pronounced features. We therefore used a different color scale to enhance their visibility. As can be seen from this figure, all structures revealed by theory can be uniquely recognized in the experiment, albeit with somewhat lower contrast. Again, only a certain pattern in the distributions appears six times (at the positions of the green dots), whereas all other structures appear eight or twelve times. Consequently, the former can be unambiguously assigned to the positions of the six F atoms, which in this case act both as emitters and scatterers.

V. CONCLUSIONS

Motivated by an earlier theoretical work [16], we explored the possibility of imaging the highly symmetric SF₆ molecule using polarization-averaged molecular-frame

photoelectron angular distributions for S 1s and F 1s photoelectrons with intermediate kinetic energies of 28 and 38 eV. The measurements were performed at the synchrotron radiation facility PETRA III at DESY employing a COLTRIMS reaction microscope for coincident particle detection, while the calculations were performed using the single-center method and code. The present experimental and theoretical PA-MFPADs agree well with each other, and for S 1s ionization, both also agree with the available theoretical predictions of Ref. [16] made for somewhat lower photoelectron kinetic energies (by about 10 eV). Even when the present PA-MFPADs do not directly image molecular bonds via forward-scattering lobes pointing toward heavy neighbors, taking into account the known octahedral molecular symmetry, it was possible to assign specific structures in the distributions to the positions of the six F atoms for all considered electron energies and emitters.

ACKNOWLEDGMENTS

We acknowledge DESY (Hamburg, Germany), a member of the Helmholtz Association HGF, for the provision of experimental facilities. Parts of this research were carried out at PETRA III and we would like to thank J. Seltmann and M. Hoesch for assistance in using beamline P04. Beamtime was allocated for Proposal No. I-20210955. The calculations were supported through the Maxwell computational resources operated at DESY. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) and Bundesministerium für Forschung, Technologie und Raumfahrt (BMFT, Federal Ministry of Research, Technology and Space). F.T. acknowledges funding by the DFG–Project No. 509471550, Emmy Noether Programme. N.M.N., N.D., and P.V.D. acknowledge funding by the DFG–Project No. 492619011 (DE 2366/6-2).

DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

-
- [1] A. Landers, Th. Weber, I. Ali, A. Cassimi, M. Hattass, O. Jagutzki, A. Nauert, T. Osipov, A. Staudte, M. H. Prior, H. Schmidt-Böcking, C. L. Cocke, and R. Dörner, Photoelectron diffraction mapping: Molecules illuminated from within, *Phys. Rev. Lett.* **87**, 013002 (2001).
 - [2] T. Jahnke, Th. Weber, A. L. Landers, A. Knapp, S. Schössler, J. Nickles, S. Kammer, O. Jagutzki, L. Schmidt, A. Czasch, T. Osipov, E. Arenholz, A. T. Young, R. Díez Muiño, D. Rolles, F. J. G. de Abajo, C. S. Fadley, M. A. Van Hove, S. K. Semenov, N. A. Cherepkov, *et al.*, Circular dichroism in K -shell ionization from fixed-in-space CO and N₂ molecules, *Phys. Rev. Lett.* **88**, 073002 (2002).
 - [3] J. B. Williams, C. S. Trevisan, M. S. Schöffler, T. Jahnke, I. Bocharova, H. Kim, B. Ulrich, R. Wallauer, F. Sturm, T. N. Rescigno, A. Belkacem, R. Dörner, Th. Weber, C. W. McCurdy, and A. L. Landers, Imaging polyatomic molecules in three dimensions using molecular frame photoelectron angular distributions, *Phys. Rev. Lett.* **108**, 233002 (2012).
 - [4] J. B. Williams, C. S. Trevisan, M. S. Schöffler, T. Jahnke, I. Bocharova, H. Kim, B. Ulrich, R. Wallauer, F. Sturm, T. N. Rescigno, A. Belkacem, R. Dörner, Th. Weber, C. W. McCurdy, and A. L. Landers, Probing the dynamics of dissociation of methane following core ionization using three-dimensional molecular-frame photoelectron angular distributions, *J. Phys. B* **45**, 194003 (2012).
 - [5] J. Adachi, M. Kazama, T. Teramoto, N. Miyauchi, T. Mizuno, M. Yamazaki, T. Fujikawa, and A. Yagishita, C 1s photoelectron angular distributions from fixed-in-space CO molecules in the high-energy continuum ≥ 50 eV, *J. Phys. B: At. Mol. Opt. Phys.* **45**, 194007 (2012).

- [6] H. Fukuzawa, R. R. Lucchese, X.-J. Liu, K. Sakai, H. Iwayama, K. Nagaya, K. Kreidi, M. S. Schöffler, J. R. Harries, Y. Tamenori, Y. Morishita, I. H. Suzuki, N. Saito, and K. Ueda, Probing molecular bond-length using molecular-frame photoelectron angular distributions, *J. Chem. Phys.* **150**, 174306 (2019).
- [7] D. Doweck and P. Decleva, Trends in angle-resolved molecular photoelectron spectroscopy, *Phys. Chem. Chem. Phys.* **24**, 24614 (2022).
- [8] F. Krasniqi, B. Najjari, L. Strüder, D. Rolles, A. Voitkiv, and J. Ullrich, Imaging molecules from within: Ultrafast angstrom-scale structure determination of molecules via photoelectron holography using free-electron lasers, *Phys. Rev. A* **81**, 033411 (2010).
- [9] M. Kazama, T. Fujikawa, N. Kishimoto, T. Mizuno, J. I. Adachi, and A. Yagishita, Photoelectron diffraction from single oriented molecules: Towards ultrafast structure determination of molecules using x-ray free-electron lasers, *Phys. Rev. A* **87**, 063417 (2013).
- [10] R. Boll, A. Rouzée, M. Adolph, D. Anielski, A. Aquila, S. Bari, C. Bomme, C. Bostedt, J. D. Bozek, H. N. Chapman, L. Christensen, R. Coffee, N. Coppola, S. De, P. Decleva, S. W. Epp, B. Erk, F. Filsinger, L. Foucar, T. Gorkhover, *et al.*, Imaging molecular structure through femtosecond photoelectron diffraction on aligned and oriented gas-phase molecules, *Faraday Discuss.* **171**, 57 (2014).
- [11] G. Kastirke, M. S. Schöffler, M. Weller, J. Rist, R. Boll, N. Anders, T. M. Baumann, S. Eckart, B. Erk, A. De Fanis, K. Fehre, A. Gatton, S. Grundmann, P. Grychtol, A. Hartung, M. Hofmann, M. Ilchen, Ch. Janke, M. Kircher, M. Kunitski, *et al.*, Photoelectron diffraction imaging of a molecular breakup using an x-ray free-electron laser, *Phys. Rev. X* **10**, 021052 (2020).
- [12] I. Vela-Peréz, F. Ota, A. Mhamdi, Y. Tamura, J. Rist, N. Melzer, S. Uerken, G. Nalin, N. Anders, D. You, M. Kircher, C. Janke, M. Waitz, F. Trinter, R. Guillemin, M. N. Piancastelli, M. Simon, V. T. Davis, J. B. Williams, R. Dörner, *et al.*, High-energy molecular-frame photoelectron angular distributions: A molecular bond-length ruler, *Phys. Chem. Chem. Phys.* **25**, 13784 (2023).
- [13] D. M. Haubenrei, N. M. Novikovskiy, M. Kircher, M. S. Schöffler, R. Dörner, T. Jahnke, and Ph. V. Demekhin, Chiral recognition with high-energy photo- and Compton electrons: A theoretical showcase study of methyloxirane and trifluoromethyloxirane molecules, *Phys. Rev. Lett.* **135**, 213203 (2025).
- [14] F. Ota, K. Yamazaki, D. Sébilleau, K. Ueda, and K. Hatada, Theory of polarization-averaged core-level molecular-frame photoelectron angular distributions: I. A full-potential method and its application to dissociating carbon monoxide dication, *J. Phys. B: At. Mol. Opt. Phys.* **54**, 024003 (2021).
- [15] F. Ota, K. Hatada, D. Sébilleau, K. Ueda, and K. Yamazaki, Theory of polarization-averaged core-level molecular-frame photoelectron angular distributions: II. Extracting the x-ray-induced fragmentation dynamics of carbon monoxide dication from forward and backward intensities, *J. Phys. B: At. Mol. Opt. Phys.* **54**, 084001 (2021).
- [16] E. Plésiat, P. Decleva, and F. Martín, Relationship between polarization-averaged molecular-frame photoelectron angular distributions and geometry, *Phys. Rev. A* **88**, 063409 (2013).
- [17] J. Vieffhaus, F. Scholz, S. Deinert, L. Glaser, M. Ilchen, J. Seltmann, P. Walter, and F. Siewert, The variable polarization XUV beamline P04 at PETRA III: Optics, mechanics and their performance, *Nucl. Instrum. Methods Phys. Res. Sect. A* **710**, 151 (2013).
- [18] 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).
- [19] 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).
- [20] T. Jahnke, T. 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).
- [21] O. Jagutzki, A. Cerezo, A. Czasch, R. Dörner, M. Hattas, M. Huang, V. Mergel, U. Spillmann, K. Ullmann-Pfleger, T. Weber, H. Schmidt-Böcking, and G. D. W. Smith, Multiple hit readout of a microchannel plate detector with a three-layer delay-line anode, *IEEE Trans. Nucl. Sci.* **49**, 2477 (2002).
- [22] R. M. Wood, Q. Zheng, A. K. Edwards, and M. A. Mangan, Limitations of the axial recoil approximation in measurements of molecular dissociation, *Rev. Sci. Instrum.* **68**, 1382 (1997).
- [23] Th. Weber, O. Jagutzki, M. Hattas, 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. D. Muiño, D. Rolles, F. J. G. de Abajo, C. S. Fadley, M. A. Van Hove, A. Cassimi, H. Schmidt-Böcking, *et al.*, *K*-shell photoionization of CO and N₂: Is there a link between the photoelectron angular distribution and the molecular decay dynamics? *J. Phys. B: At. Mol. Opt. Phys.* **34**, 3669 (2001).
- [24] R. N. Zare, Photoejection dynamics, *Mol. Photochem.* **4**, 1 (1972).
- [25] C. W. McCurdy, T. N. Rescigno, C. S. Trevisan, R. R. Lucchese, B. Gaire, A. Menssen, M. S. Schöffler, A. Gatton, J. Neff, P. M. Stammer, J. Rist, S. Eckart, B. Berry, T. Severt, J. Sartor, A. Moradmand, T. Jahnke, A. L. Landers, J. B. Williams, I. Ben-Itzhak, *et al.*, Unambiguous observation of F-atom core-hole localization in CF₄ through body-frame photoelectron angular distributions, *Phys. Rev. A* **95**, 011401(R) (2017).
- [26] Ph. V. Demekhin, A. Ehresmann, and V. L. Sukhorukov, Single center method: A computational tool for ionization and electronic excitation studies of molecules, *J. Chem. Phys.* **134**, 024113 (2011).
- [27] Ph. V. Demekhin, D. V. Omel’yanenko, B. M. Lagutin, V. L. Sukhorukov, L. Werner, A. Ehresmann, K.-H. Scharfner, and H. Schmoranz, Investigation of photoionization and photodissociation of an oxygen molecule by the method of coupled differential equations, *Opt. Spectrosc.* **102**, 318 (2007).
- [28] S. A. Galitskiy, A. N. Artemyev, K. Jänkälä, B. M. Lagutin, and Ph. V. Demekhin, Hartree-Fock calculation of the differential photoionization cross sections of small Li clusters, *J. Chem. Phys.* **142**, 034306 (2015).

- [29] N. M. Novikovskiy, A. N. Artemyev, D. V. Rezvan, B. M. Lagutin, and Ph. V. Demekhin, Multichannel single center method, *J. Phys. B: At. Mol. Opt. Phys.* **55**, 175001 (2022).
- [30] J. Leroux, D. Stermer, B. Credidio, F. Dudda, E. Heikura, A. Jose, A. Judt, C. Küstner-Wetekam, M. Zander, N. M. Novikovskiy, T. Otto, P. Patil, G. Petersen, S. Savio, N. Velasquez, N. Wieland, L. Wülfing, P. V. Demekhin, F. Trinter, and M. Ilchen, Oxygen-specific photoelectron circular dichroism in gas-phase fenchone, *Phys. Rev. Res.* **8**, 013340 (2026).
- [31] L. Sommerlad, N. M. Novikovskiy, F. Trinter, D. Stermer, O. D. McGinnis, A. Pier, N. Melzer, J. Kruse, M. Kircher, L. Kaiser, T. Wenzel, T. Jahnke, R. Dörner, Ph. V. Demekhin, and M. Schöffler, Revisiting giant photoelectron asymmetries in fenchone enantiomers, *Phys. Rev. Res.* (2026), doi: [10.1103/jw4j-gfd8](https://doi.org/10.1103/jw4j-gfd8).
- [32] L. S. Bartell and S. K. Doun, Structures of hexacoordinate compounds of main-group elements: Part III. An electron diffraction study of SF₆, *J. Mol. Struct.* **43**, 245 (1978).
- [33] M. W. Schmidt, K. K. Baldrige, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, Jr., General atomic and molecular electronic structure system, *J. Comput. Chem.* **14**, 1347 (1993).
- [34] T. H. Dunning, Jr., Gaussian basis functions for use in molecular calculations. III. Contraction of (10s6p) atomic basis sets for the first-row atoms, *J. Chem. Phys.* **55**, 716 (1971).
- [35] N. A. Cherepkov, S. K. Semenov, A. V. Golovin, J. Adachi, and A. Yagishita, O *K*-shell photoemission of the CO molecule: Comparison between theory and experiment, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 4803 (2004).
- [36] S. K. Semenov, N. A. Cherepkov, T. Jahnke, and R. Dörner, Theoretical study of vibrationally resolved photoionization for the C *K*-shell of the CO molecule, *J. Phys. B: At. Mol. Opt. Phys.* **37**, 1331 (2004).
- [37] P. V. Demekhin, Tutorial: Angle-resolved photoionization of molecules, *J. Phys. B: At. Mol. Opt. Phys.* **59**, 053001 (2026).
- [38] C. A. Marante, L. Greenman, C. S. Trevisan, T. N. Rescigno, C. W. McCurdy, and R. R. Lucchese, Validity of the static-exchange approximation for inner-shell photoionization of polyatomic molecules, *Phys. Rev. A* **102**, 012815 (2020).
- [39] See Supplemental Material at <https://link.aps.org/supplemental/10.1103/68bc-m3y9> for interactive three-dimensional emission distributions from Figs. 1–3(c) and 1–3(d) that can be rotated using a mouse cursor.