Role of a Neighbor Ion in the Fragmentation Dynamics of Covalent Molecules

A. Méry,[1,*] A. N. Agnihotri,[1] J. Douady,[1] X. Fléchard,[2] B. Gervais,[1] S. Guillous,[1] W. Iskandar,[3] E. Jacquet,[1] J. Matsumoto,[4] J. Rangama,[1] F. Ropars,[1] C. P. Safvan,[5] H. Shiromaru,[4] D. Zanuttini,[1] and A. Cassimi[1]

[1]*CIMAP, CEA-CNRS-ENSICAEN-UNICAEN, Normandie Université, BP5133, F-14050 Caen Cedex 04, France*
[2]*Normandie Univ, ENSICAEN, UNICAEN, CNRS/IN2P3, LPC Caen, 14000 Caen, France*
[3]*Chemical Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*
[4]*Department of Chemistry, Tokyo Metropolitan University, 1-1 Minamiosawa, Hachiouji-shi, Tokyo 192-0397, Japan*
[5]*Inter University Accelerator Center, Aruna Asaf Ali Marg, New Delhi 110067, India*

Fragmentation of molecular nitrogen dimers $(N_2)_2$ induced by collision with low energy 90 keV Ar^{9+} ions is studied to evidence the influence of a molecular environment on the fragmentation dynamics of N_2 cations. Following the capture of three or four electrons from the dimer, the three-body $N_2^+ + N^{m+} + N^{n+}$ [with $(m, n) = (1, 1)$ or $(1, 2)$] fragmentation channels provide clean experimental cases where molecular fragmentation may occur in the presence of a neighbor molecular cation. The effect of the environment on the fragmentation dynamics within the dimer is investigated through the comparison of the kinetic energy release (KER) spectra for these three-body channels and for isolated $N_2^{(m+n)+}$ monomer cations. The corresponding KER spectra exhibit energy shifts of the order of 10 eV, attributed to the deformation of the $N^{m+} + N^{n+}$ potential energy curves in the presence of the neighboring N_2^+ cation. The KER structures remain unchanged, indicating that the primary collision process is not significantly affected by the presence of a neighbor molecule.

Weakly bound systems offer a unique tool to investigate the transition from gas phase isolated atoms or molecules to the condensed phase. Over the past decades, a large amount of experimental and theoretical work has been conducted to understand the properties of clusters spanning a large range of sizes and constituents. Rare gas dimers are of particular interest as they offer a simple system consisting of two neighbor quasi-independent atoms where the electrons remain localized on each atom resulting in a very low electron mobility across the dimer [1]. This specific property has enabled access to site sensitive decay processes by retaining the memory of the initial capture processes [2]. Low electron mobility also leads to specific deexcitation processes enabled by the presence of the neighbor atom. Among these, interatomic Coulomb decay has been thoroughly studied as the resulting emission of a low energy electron may be responsible for extensive radiation damage in matter [3–6]. In clusters of complex molecules, the surrounding molecules may act as a protective environment by dissipating the transferred excitation energy among the degrees of freedom available in the cluster. As an example, in amino acid clusters, it has been shown that preferential breaking of intermolecular hydrogen bonds significantly prevents intramolecular fragmentation from occurring [7]. Recently, it has also been demonstrated that ion irradiation of fullerene or polycyclic aromatic hydrocarbon clusters can drive the formation of new chemical bonds leading to the formation of larger covalent molecules [8,9]. By contrast, dimers formed by

two diatomic molecules are small clusters of intermediate complexity for which the three-body combined intramolecular and intermolecular dissociation following multi-ionization has never been studied thoroughly. Precise measurement of this three-body fragmentation process provides crucial information on the role of a neighbor molecule for both primary excitation processes and fragmentation dynamics. Very recently, the three-body fragmentation of $(CO_2)_2$ dimers has been investigated via multiple ionization by intense femtosecond laser pulses [10]. In this particular case, three-body fragmentation appears as a sequential dissociation where the covalent $C = O$ bond breaks on a longer time scale than the weak van der Waals bond.

We consider here dimers of the simple diatomic N_2 molecule, which constitutes a model system of polyatomic complex containing both covalent intramolecular bonds and van der Waals intermolecular bonds. The first evidence of $(N_2)_2$ dimers at 77 K temperature was found using infrared spectroscopy more than 40 years ago [[11,12]. More recently, quantum chemistry calculations have predicted the existence of several isomeric states of the ground state of $(N_2)_2$ that correspond to different geometrical alignment of the constitutive molecules with respect to the dimer axis [13,14].

In the present work, slow highly charged ions and $(N_2)_2$ targets are used to produce $(N_2)_2^{q+}$ ionized dimers. A cold target recoil ion momentum spectroscopy (COLTRIMS) setup [15] allows us to measure in coincidence the time of

arrival and positions of the positively charged fragments resulting from the collision between the $(N_2)_2$ dimer target and Ar^{9+} projectile ions. The $(N_2)_2$ target is produced using the supersonic expansion of N_2 through a 30 μm nozzle at a pressure of 25 bars at room temperature. The proportion of $(N_2)_2$ dimers inside the gas jet is estimated to be a few percent. A continuous beam of Ar^{9+} projectiles is extracted from the electron cyclotron resonance ion source of the ARIBE-GANIL facility with energy of 90 keV and is collimated by a 600 μm diameter aperture located in front of the spectrometer. The target and projectile beams cross at a right angle at the center of the spectrometer where a homogeneous perpendicular electric field (40 V/cm) ensures a 4π collection of singly charged ions up to 16 eV on a 80 mm diameter microchannel plate (MCP) coupled to delay-line anodes. The final charge state of the projectile ions is determined using an electrostatic parallel plates analyzer located after the spectrometer. Projectile ions with final charge states from $8+$ to $5+$ are discriminated using a dedicated MCP detector coupled to delay-line anodes. Detection of the projectile ion also provides the start for the time-of-flight measurement of the recoiling ions in the spectrometer. For each event corresponding to two-body or three-body fragmentation, the three-dimensional position of the collision is inferred from the data using momentum conservation laws and is used to select the desired fragmentation channel while suppressing accidental coincidences. Moreover, by reconstructing the fragments momentum in the center of mass of the fragmenting target, momentum resolution is no longer limited by the size of the collision area. An important point is that the gas jet contains both monomers and dimers. Therefore the comparison between monomer and dimer fragmentation is performed using the same data set.

At the low collision energy chosen for the present study, electron capture is dominant and the $(N_2)_2^{q+}$ ions are mainly produced in the ground and low excited states [16]. Moreover, thanks to the large capture radii of the projectile ion, electron capture may take place from one or two molecular sites of the dimer depending on the impact parameter and orientation of the dimer with respect to the projectile trajectory [1,2]. When electrons are removed from each site of the dimer, Coulomb explosion leads to the cleavage of the weak van der Waals bond. If two or more electrons are removed from one site, most commonly the corresponding molecular ion also breaks up. The relevant fragmentation channels are referred to as

$$N_2^{2+} \rightarrow N^+ + N^+, \tag{1a}$$

$$N_2^{3+} \rightarrow N^{2+} + N^+, \tag{1b}$$
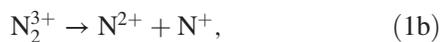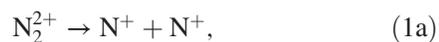
where Eq. (1a) [respectively (1b)] corresponds to the two-body dissociation of the dication (respectively trication) from the monomer target N_2, and

$$(N_2)_2^{3+} \rightarrow N_2^+ + N^+ + N^+, \tag{2a}$$

$$(N_2)_2^{4+} \rightarrow N_2^+ + N^{2+} + N^+, \tag{2b}$$
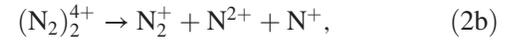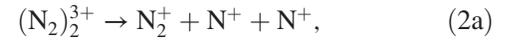
where Eq. (2a) [respectively (2b)] corresponds to the similar three-body dissociation of the dication (respectively trication) but from the dimer target $(N_2)_2$.

Fragmentation of the N_2 molecule has been extensively studied using electron impact [17,18], proton impact [19], ion impact [20], and photoionization [21,22]. The Doppler-free kinetic energy release (KER) of the dissociating dication N_2^{2+} has been measured allowing the identification of the main populated states of the transient molecular ion [17]. Considering $(N_2)_2$ dimers, the relevant three-body fragmentation channels [Eqs. (2a) and (2b)] constitute model cases where the presence of the recoiling neighbor N_2^+ molecular ion may affect the fragmentation of the adjacent molecular cation: after the collision, the intense electric field generated by the neighbor N_2^+ ion modifies the $N^{m+} + N^{n+}$ potential energy curves. As a consequence, the transient states populated prior fragmentation and the corresponding energy release provide a signature of these modifications. Results from these particular channels of the dimer are directly compared to the fragmentation of the monomer [Eqs. (1a) and (1b)]. Theoretical *ab initio* calculations of the potential energy curves associated to the intermediate state $(N_2)_2^{3+}$ give new insight into the influence of a spectator ion on the dissociation dynamics of the N_2^{2+} dication. In three-body fragmentation, the length of the van der Waals bond in the $(N_2)_2$ neutral dimer is crucial as it fixes the strength of the electric field acting on the dissociating dication or trication [Eq. (1a) or (1b)]. This equilibrium intermolecular distance is deduced from the $(N_2)_2^{2+} \rightarrow N_2^+ + N_2^+$ fragmentation channel that corresponds to single electron capture on each molecule of the dimer followed by the cleavage of the van der Waals bond. The associated KER spectrum contains one main peak centered at 3.35±0.1 eV. Assuming a pure Coulomb explosion, the equilibrium intermolecular distance in the dimer is found to be $R_e = 4.30 \pm 0.13$ Å. This value agrees very well with the former experimental measurement involving resonant core excitation followed by the intermolecular coulomb decay process [5] and with the theoretical calculations from [[13,14]. It is worth noting that the relative orientation of the two N_2 molecules inside the dimer also influences the fragmentation dynamics for three-body channels. Nevertheless, as the size of the N_2 molecule is small compared to the length of the van der Waals bond, molecular orientation is expected to have a very limited influence for the present discussion (see later in the text). Figures (1a) and (1b) present the KER spectra for the fragmentation of the nitrogen dication and trication from monomers that are highly dominant inside the jet target. The resolution of our apparatus enables the identification of
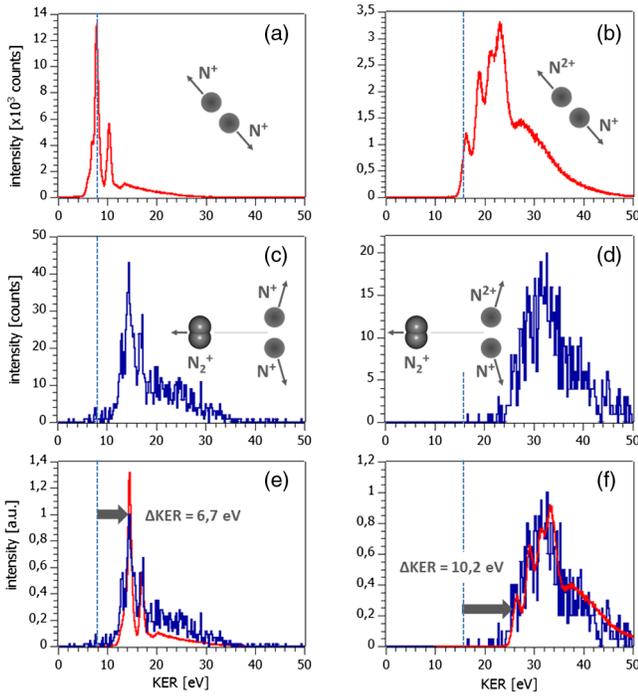
FIG. 1.   KER spectra for (a) $N^+ + N^+$, (b) $N^+ + N^{2+}$ from monomers, and (c) $N_2^+ + N^+ + N^+$, (d) $N_2^+ + N^+ + N^{2+}$ from dimers. [(e) and (f)] Superposition of the three-body and the normalized two-body KER spectra shifted by 6.7 eV (respectively 10.2 eV).

several transient states of the N_2^{2+} dication. Two main peaks are identified at KER values of about 7.8 and 10.3 eV corresponding to specific states of the transient N_2^{2+} dication [17]. For the $N^+ + N^{2+}$ channel, the KER spectrum also exhibits several peaks associated to different molecular states of the trication.

The KER spectra of the three-body dissociation channels following multiple ionization of the dimer are presented in Figs. (1c) and (1d) where the KER value includes the kinetic energy of the three fragments in the dimer center-of-mass frame. Figures (1a) and (1c) show that the relative population of the main peaks associated to the $N^+ + N^+$ channel is only slightly modified by the presence of the N_2^+ ion, but a global energy shift of about 6.7 eV is observed when comparing the monomer and dimer fragmentation channels [Fig. (1e)]. This indicates that the capture processes and the resulting populated states of the dication are weakly modified by the presence of the neighbor N_2^+ ion. Indeed, due to the large intermolecular distance, the two molecules of the dimer can be considered as quasi-independent; i.e., there is a negligible sharing of the orbitals of the two constitutive N_2 molecules. In a first approximation, the measured shift in the KER spectra may thus be interpreted as the amount of potential energy added to the system in the presence of the second N_2^+ ion. In such a simple picture we can calculate the KER difference between two- and three-body channels by using pure

Coulomb potential energy curves. We assume the equilibrium internuclear distance in the N_2 molecule to be $R_{N-N} = 1.1$ Å and the van der Waals bond length to be $R_e = 4.3$ Å (as described earlier). The N_2^+ ion is also approximated to a pointlike particle located at its center of mass. The additional potential energy results from the repulsive interaction between the recoiling N_2^+ ion and the two N^{m+} and N^{n+} ions (where $m = 1$ and $n = 1$ or 2). It comes as

$$\Delta KER = \frac{e^2}{4\pi\epsilon_0}\left(\frac{m}{R_{N_2^+-N^{m+}}} + \frac{n}{R_{N_2^+-N^{n+}}}\right) \quad (3)$$

where the subscripts m and n refer to the charge state of each atomic ion. Note that, due to the large intermolecular distance compared to the molecular size, the expected energy shift is poorly dependent on the initial orientation of the molecules inside the dimer and can roughly be estimated to scale with $1/R_e$. Using $R_e = 4.3$ Å and assuming molecules initially perpendicular to the dimer axis, this gives

$$\Delta KER \cong (m + n) \times 3.32 \text{ eV}. \quad (4)$$

For channels 1a and 2a, the calculated value $\Delta KER = 6.64$ eV fits nicely with the observed 6.7 eV shift obtained by adjusting the experimental two-body and three-body KER spectra [Fig. (1e)]. We apply the same comparison for the fragmentation of the trication from the monomers and dimers [Eqs. (1b) and (2b)]. Even though statistics is much lower for these channels, similar conclusions can be extracted. Again, we observe that the KER spectrum is globally shifted towards higher energies due to the presence of the neighboring N_2^+ ion [Fig. (1f)]. The measured experimental shift of about 10.2 eV for the $N^{2+} + N^+$ channel is also consistent with the Coulomb model $\Delta KER \cong 3 \times 3.32 = 9.96$ eV.

These comparisons of the fragmentation dynamics of N_2^{2+} and N_2^{3+} molecular ions with or without a neighbor cation can thus be interpreted as follows. The neighbor molecule does not influence significantly the relative populations of the molecular ion transient states following the electron capture process. However, the Coulomb electric field due to the presence of a N_2^+ cation modifies the potential energy curves of the N_2^{2+} and N_2^{3+} molecular ions, resulting in a shift of the KER spectra towards higher energies. Moreover, this shift is quantitatively reproduced by considering the additional potential energy due to the third electric charge N_2^+ located at the equilibrium distance of the neutral dimer. Note that, within this classical model, the expected energy shift is null in the case of the presence of a neutral neighbor (which is not accessible with our experimental method). This is a strong indication that multi-ionization in N_2 clusters may be simply treated as successive and independent collisions with neighboring diatomic molecules, whose fragmentation energy is only
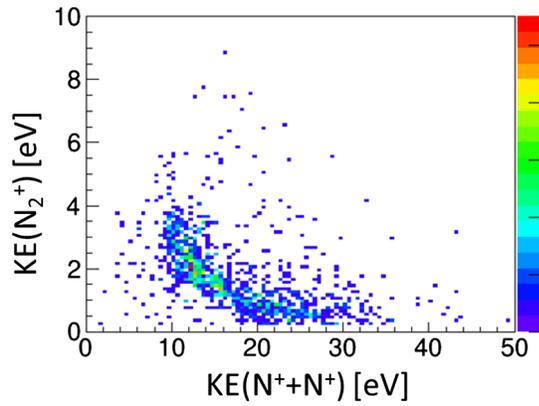
FIG. 2.   Kinetic energy of the N_2^+ molecular ion as a function of the sum of the kinetic energies of the two N^+ ions for three-body fragmentation [Eq. (2a)].

affected by the resulting charge distribution on neighbor molecules. This observation constitutes a crucial starting point for understanding the fragmentation dynamics of more complex clusters.

To get further details of the three-body dissociation dynamics, the sharing of the total KER among the three emitted ions has also been investigated for the channel 2a (Fig. 2). It appears that the N_2^+ molecular ion acquires a kinetic energy ranging from 0.5 to 4 eV depending on the kinetic energy of the two N^+ fragments. The correlation plot (Fig. 2) shows that the more energetic the fragmentation of the dication is the less energy is transferred to the N_2^+ ion. In other words, the N_2^+ ion spends a shorter time in the electric field of the fragmenting $N^+ + N^+$ and thus acquires smaller energy. For this channel [Eq. (1a)], the total energy shift of 6.7 eV is distributed among the three particles and a mean value of about 1.7 eV is given to the N_2^+ ion while the remaining 5 eV are shared as extra kinetic energy between the two N^+ ions.

To confirm the previous analysis of the KER measurement of the three-body dissociation channel [Eq. (2a)], we also investigate the potential energy surface of the $(N_2)_2^{3+}$ by means of *ab initio* calculation. As discussed above, the length between the two N_2 molecules is sufficiently large and their interaction is essentially electrostatic. We therefore consider only the dissociation of N_2^{2+} in the field of the idealized N_2^+ which is represented by a simple point charge at its center of mass. Despite the corresponding significant reduction of the computational workload, the evaluation of the whole three-dimensional potential energy surfaces (PESs) of the N_2^{2+} dication in a point-charge electric field is still cumbersome. It is further simplified by considering only T-shaped geometries of C_{2v} symmetry, with the point charge in the symmetry plane of the N_2^{2+} molecule. A second-order configuration interaction calculation using MOLCAS quantum chemistry package [23] with the *aug-cc-p* VQZ basis set [24,25] has been performed as follows. The reference space is made of six molecular orbitals correlating
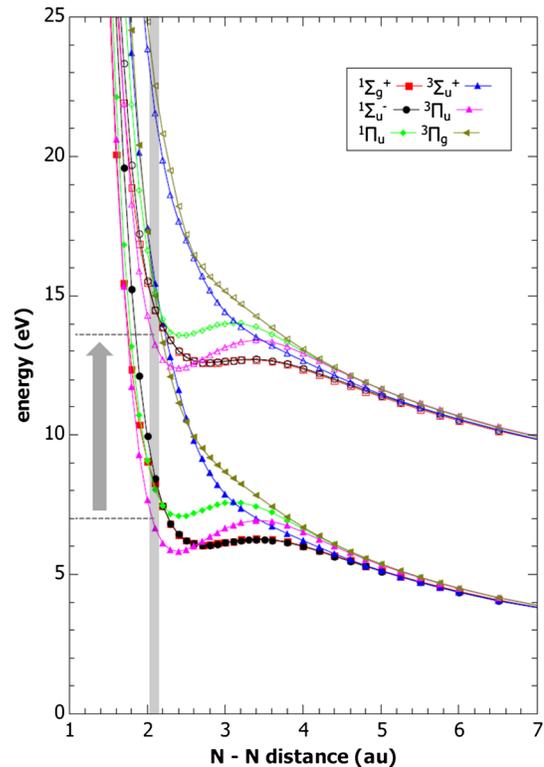
FIG. 3.   Calculated potential energy curves of the N_2^{2+} dication without (full symbols) and within the electric field created by a point charge N_2^+ ion located at 4.3 Å (open symbols). The asymptotic limit for all PECs has been fixed to 0 eV. The gray band corresponds to the Franck-Condon region and the upward arrow illustrates the shift of the PECs in the presence of the neighbor N_2^+ ion. The shift is approximately 6.7 eV for all the different states of the dication.

asymptotically with the $2p$ orbitals of the N atoms. These molecular orbitals are optimized at each intermolecular distance by means of a state-average complete active-space self-consistent field calculation. Once the orbitals have been optimized, they are used to build up a set of symmetry-adapted configurations, all used as references to generate a much larger space made of all singly and doubly excited configurations. The molecular Hamiltonian is then diagonalized in this large configuration space to obtain accurate PESs. All the potential energy curves (PECs) associated with the $N^+ + N^+$ dissociation limits were generated, first without any point charge [Eq. (1a)], and then with a charge located at $R_e = 4.3$ Å from the N_2^{2+} dication center of mass [Eq. (2a)], to find out the electric field effects.

Some of the curves correlating to the lowest dissociation limit are depicted in Fig. 3. The main effect of the neighbor N_2^+ molecule is to shift upward the PESs in the Franck-Condon area by an energy amount corresponding approximately to the Coulomb repulsion between 1+ and 2+ point charges at the initial distance (i.e., $(2 \times 27.21)/R_e \approx$ 6.7 eV). As the stretch of the dication increases, the

Coulomb repulsion diminishes and the two series of curves merge asymptotically. The relative positions of the PESs are only marginally perturbed by the presence of the neighbor N_2^+ molecule. We emphasize that for a dissociation process, the KER depends only on the initial and final potential energies and not on the details of trajectories. Therefore, the shift observed in Fig. 3 reflects the KER modification due to the neighbor N_2^+ molecule. Since all the PESs are perturbed in a very similar way, only a global shift of the KER value is induced by the neighbor molecule, as observed experimentally.

Molecular fragmentation of diatomic N_2 dimers enabled a precise study of the role of the environment on the fragmentation of the constitutive molecules. Because of the large intermolecular distance, the primary collision process as well as molecular fragmentation is shown to be poorly affected by the presence of a second spectator ion. Theoretical calculations have shown that the electric field generated by the neighbor ion does not significantly modify the potential energy curves of the dication. The measured shift in the three-body KER spectra results mainly from the additional electrostatic potential energy provided by the N_2^+ partner. The shift is of the order of a few eV and depends only on the intermolecular distance and charge states of the fragments. This new picture of the molecular fragmentation dynamics for N_2 dimers constitutes an important step for the understanding of the role of the environment in the irradiation and fragmentation of van der Waals clusters relevant for biology and astrophysics.

Note added.—Recently, results on the three-body fragmentation of CO dimers induced by intense ultrashort laser pulses were published [26]. Similar shifts of the KER spectra are reported and the appearance of an exotic fast dissociation channel of the CO^{2+} dication is observed.

---

[*]mery@ganil.fr
[1] J. Matsumoto, Phys. Rev. Lett. **105**, 263202 (2010).
[2] W. Iskandar, Phys. Rev. Lett. **113**, 143201 (2014).
[3] T. Jahnke, Nat. Phys. **6**, 139 (2010).
[4] H. Kim, Phys. Rev. A **88**, 042707 (2013).
[5] F. Trinter, Nature (London) **505**, 664 (2014).
[6] W. Iskandar, Phys. Rev. Lett. **114**, 033201 (2015).
[7] S. Maclot, J. Phys. Chem. Lett. **4**, 3903 (2013).
[8] H. Zettergren, Phys. Rev. Lett. **110**, 185501 (2013).
[9] R. Delaunay, J. Phys. Chem. Lett. **6**, 1536 (2015).
[10] Y. Fan, Chem. Phys. Lett. **653**, 108 (2016).
[11] C. Long, Chem. Phys. **2**, 485 (1973).
[12] A. McKellar, J. Chem. Phys. **88**, 4190 (1988).
[13] V. Aquilanti, J. Chem. Phys. **117**, 615 (2002).
[14] L. Gomez, Chem. Phys. Lett. **445**, 99 (2007).
[15] J. Ullrich, J. Phys. B **30**, 2917 (1997).
[16] B. Walch, Phys. Rev. Lett. **72**, 1439 (1994).
[17] M. Lundqvist, J. Phys. B **29**, 1489 (1996).
[18] A. Pandey, J. Chem. Phys. **140**, 034319 (2014).
[19] O. Furuhashi, Chem. Phys. Lett. **337**, 97 (2001).
[20] J. Rajput, Phys. Rev. A **74**, 032701 (2006).
[21] S. Hsieh, J. Phys. B **29**, 5795 (1996).
[22] T. Weber, J. Phys. B **34**, 3669 (2001).
[23] F. Aquilante, J. Comput. Chem. **31**, 224 (2010).
[24] T. Dunning, J. Chem. Phys. **90**, 1007 (1989).
[25] R. Kendall, J. Chem. Phys. **96**, 6796 (1992).
[26] X. Ding, M. Haertelt, S. Schlauderer, M. S. Schuurman, A. Yu. Naumov, D. M. Villeneuve, A. R. W. McKellar, P. B. Corkum, and A. Staudte, Phys. Rev. Lett. **118**, 153001 (2017).