

Ratiometric Comparison of Intense Field Ionization of Atoms and Diatomic Molecules

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Intense-laser ionization rates for rare gas atoms and diatomic molecules have been precisely compared by making simultaneous measurements of ionization yield vs laser intensity for mixed atomic and molecular targets. At a given laser intensity, the N₂ and F₂ ionization yields are slightly greater than that of Ar. Conversely, comparison of O₂ and S₂ with Xe indicates significant ionization suppression in these molecules. Recent molecular ionization models that successfully describe ionization suppression in O₂ and its absence in N₂ fail to explain our observations in F₂ and S₂.

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Currently, there is great interest in exploiting the nonperturbative interaction between molecules and intense lasers to investigate a variety of problems of basic scientific and practical importance. For example, strong laser fields may be employed to manipulate inter- and intramolecular dynamics as well as orient, steer, and focus molecular beams [1,2]. In addition, intense lasers may be used as “soft” ionizers [3,4], enabling sophisticated mass spectrometry of large molecules. Further development of these and other applications of intense lasers to interrogate and manipulate molecules requires an accurate understanding of molecular behavior in strong laser fields.

Quantum calculations of strong-field atomic ionization, based on the single active-electron (SAE) approximation, have been extremely successful in predicting total and differential ionization yields [5]. Unfortunately, due to their additional complexity, analogous treatments in molecules are not readily available. Instead, strong-field molecular ionization is commonly treated using more approximate tunneling [6] or multiphoton [7] models. To lowest order, these methods predict ionization rates that depend only on laser wavelength and intensity, and the ionization potential of the species of interest. Because these theories have been fairly successful in describing total ionization yields in atoms, it is not unreasonable to expect that similar models might capture the essence of molecular ionization as well, particularly in the case of diatomics.

Indeed, early measurements indicated that intense-laser ionization rates of diatomics are nearly equal to those of atoms with similar electron binding energies [8]. In more recent work, however, the ionization yield of O₂ was found to be suppressed, by an order of magnitude, relative to Xe, an atom with nearly the same ionization potential as O₂ [9,10]. Following these observations, several mechanisms were proposed to explain this presumably anomalous behavior [9,11–13]. At best, these provided only qualitative agreement with observation.

However, in a recent Letter [14], Guo introduced a charge-screening correction to tunnelling theory that, when

used with the appropriate parameters, fits the observed suppression of O₂ ionization. In an adjacent Letter [15], Muth-Böhm *et al.* suggest that interference between electrons emitted from the vicinity of two distinct ionic cores leads to suppressed ionization in diatomic species with antisymmetric electronic ground states. Their calculations correctly describe the suppressed ionization of O₂, the absence of suppression in N₂, and also predict ionization suppression of F₂ [15]. The screening [14] and interference [15] mechanisms, as presented, are quite general and presumably apply to all diatomic and even larger molecules. Calculations based on these models could be extremely useful, providing approximate yet accurate intense-field ionization rates for molecules. However, at present, the generality of these approaches is based on the extrapolation of their successful description of ionization in just two diatomic species, O₂ and N₂. The primary motivation for our experiments is to provide further experimental tests of the models.

Measuring the relative ionization rates of different species is actually quite challenging, due to the rapid growth of ionization yields with increasing laser intensity [10,16]. When ionization yields from single species targets are measured serially, small changes in the laser intensity or alignment can produce significant systematic errors. For example, shifting the intensity scale of our N₂⁺ data by 10% changes the N₂:Ar ionization ratio at 1×10^{14} W cm⁻² from 1.90 to 0.93. Furthermore, due to the design of many spectrometers, small changes in the position of the laser focus, caused by nominal beam alignment or beam pointing fluctuations, can alter the ion collection efficiency and lead to sizable errors in the measured ionization ratios.

We have circumvented both of these issues by simultaneously measuring ionization yields from mixed atomic and molecular targets. This technique increases the accuracy of the yield ratio determinations by reducing the need for precise run to run control of the laser intensity and alignment. In this Letter, we report the results of high

precision measurements of the ratio of single ionization yields in molecular species (F_2 , S_2 , N_2 , and O_2) to those in atomic targets (Xe and Ar) of similar IP. *Our results clearly indicate that the two models, which successfully predict the anomalous behavior of O_2 [14,15], do not adequately describe intense-laser ionization of diatomic molecules in general.*

In our experiments, low density gas targets are exposed to a focused laser beam in a high vacuum chamber with a base pressure of approximately 5×10^{-10} torr. Single ion events are gathered via time-of-flight (TOF) mass spectrometry with a chevron microchannel plate (MCP) detector, and recorded with a multichannel scaler (MCS) that is capable of counting multiple events per trigger. The sample pressures are adjusted to ensure, at all laser intensities, a count rate of less than one event per trigger in any ion channel. Uniform detection efficiency of all ions is ensured by accelerating them to greater than 4 kV before impacting the detector, and by reducing the lower MCS discriminator to a level where the measured $Xe^{2+}:Xe^+$ ratio is found to be independent of the discriminator setting. Thus, ionization events from different species are detected with identical efficiencies.

All targets except S_2 are available as bottled gases. These are introduced into the vacuum chamber using separate leak valves for the atomic and molecular species, respectively. Sample partial pressures are measured with a residual gas analyzer (RGA) and corrected for electron impact ionization cross section [17]. The accuracy of this pressure measurement was confirmed by repeating several ionization measurements using gas mixtures [9,10]. Ar (99 torr) and N_2 (156 torr) were combined with He at a total pressure of approximately 2580 torr, producing a 0.042:0.067:1 mixture of Ar: N_2 :He. The Ar: N_2 pressure ratio measured using the RGA agreed with the known ratio in the prepared mix to within 4%. The concentration of the F_2 sample, a 5% commercial mixture in He, was also verified by RGA measurement.

S_2 vapor is created by heating iron pyrites (FeS_2) in a separately pumped chamber and introduced to the TOF chamber through a 1 mm pinhole [18]. The pinhole is not aligned with either the RGA or the ionization region so that measured RGA and TOF signals are due to the diffuse S_2 background gas, not from an S_2 beam. By varying the temperature of the oven, the S_2 partial pressure in the TOF chamber can be adjusted from approximately 10^{-9} to 10^{-6} torr [18].

Intense, 2 mJ, 790 nm, 100 fs laser pulses are produced by an amplified Ti:sapphire laser operating at a 1 kHz repetition rate. The pulse energy at the experiment is continuously tunable using a half-wave plate and polarizing beam splitter. The laser is focused into the target gases using either a Crown glass lens or a gold mirror with 30 and 5 cm focal lengths, respectively. The absolute ion yield from each target is quite sensitive to focusing geometry and alignment of the laser focus with the TOF spectrometer.

However, we find that the ratio of ionization yields, from simultaneously irradiated atomic and molecular species, is insensitive to the specific focusing optic used and to the precise position of the laser focus relative to a 1 mm extraction slit at the entrance to the TOF spectrometer.

At each laser intensity, data are collected for 10^5 to 10^7 laser shots. The integrated yield in each observed ion peak is recorded. This yield is then divided by the number of laser shots, and by the partial pressure of target gas to obtain the ionization probability for each target species in units of counts/(shot torr). While single ionization is by far the dominant process observed, at the highest intensities, double and dissociative ionization cannot be neglected. These additional channels are handled in one of two ways. In most cases, the dissociative and double ionization yields are simply added to the single ionization channel. However, because S^+ counts cannot be distinguished from the O_2^+ signal produced by ionization of residual O_2 in the chamber, it is difficult to determine a precise S^+ yield. The uncertainty in the S^+ dissociative ionization yield is included in the error bars on Fig. 1. Also, F_2 reacts with small amounts of residual water and/or hydrocarbons to produce HF. While the contaminant fraction is small relative to the F_2 concentration, it leads to uncertainty in the origin of F^+ ions, which is reflected in the error bars of Fig. 2. Once the total ionization yields of the respective targets have been determined, they are divided to obtain the ratio of molecular to atomic ionization. It should be emphasized that the primary sources of error in our determinations are due to statistics and the uncertainty in the partial pressure determination ($\sim 5\%$), not from double ionization or fragmentation processes. The absolute ionizing intensities are determined by the onset of double ionization for the noble gases [10].

As shown in Fig. 1, our measurement of the intensity dependence of the $O_2:Xe$ ionization ratio is consistent with previous results [10]. At low intensities, the total ion yield of O_2^+ remains nearly constant at a value between 0.15 and 0.2 times that of Xe. Above 10^{14} $W\text{cm}^{-2}$, saturation of the Xe yield results in an increase of the ionization ratio. Above 5×10^{14} $W\text{cm}^{-2}$ both species ionize with near 100% efficiency and the ratio saturates at unity [19].

The $N_2:Ar$ ionization ratio determinations are shown in Fig. 2. A survey of the recent literature finds significant discrepancies between the various determinations of the $N_2:Ar$ yield ($N_2:Ar \approx 0.7$ [10], 0.2 [16], 1 [20], 1.7 [our results]). Importantly, there are significant differences in the pulse durations used in the different experiments (30 fs [10], 200 fs [16], 50 fs [20], and 100 fs [our results]), and recent calculations suggest that the $N_2:Ar$ ionization ratio has a notable pulse-duration dependence [15]. However, it should also be noted that the potential for error in determining the ionization yield ratio from single rather than dual species targets is more severe for $N_2:Ar$ since the slope of the ionization vs intensity curve is considerably steeper for these higher IP species. Our ratiometric determinations

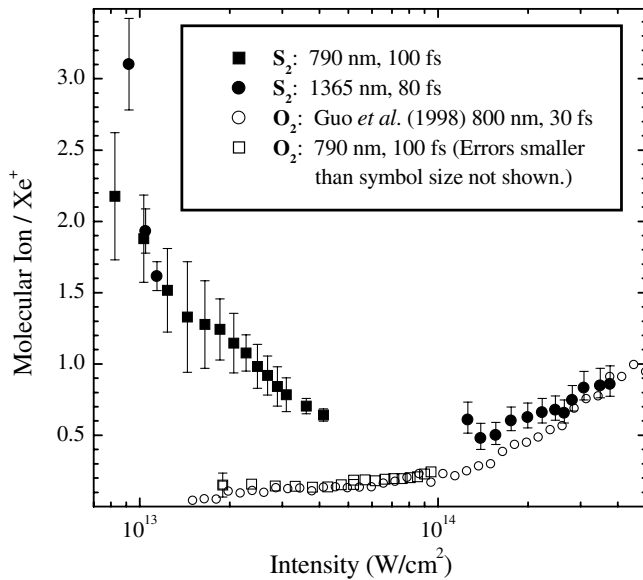


FIG. 1. The ratios of O_2^+ (IP = 12.06 eV) and S_2^+ (IP = 9.36 eV) to Xe^+ (IP = 12.13 eV) as a function of laser intensity. The O_2^+ data of Guo *et al.* [10] are shown without their detection efficiency correction [19]. Over the intensity range shown, the ionization yields of the S_2^+ and Xe^+ vary by factors of ≈ 1500 for the 790 nm data and ≈ 1000 for the 1365 nm S_2^+ : Xe^+ data. For the O_2^+ : Xe^+ data, the O_2^+ and Xe^+ ionization yields vary by factors of 3×10^4 and 2.4×10^4 , respectively. Because of the disparity in IPs between S_2 and Xe , the observed ionization ratio of order unity indicates significant suppression of S_2^+ production.

indicate that the N_2 : Ar ratio for 100 fsec 780 nm pulses is nearly constant at approximately 1.7, before falling towards unity near the saturation intensity.

The F_2 : Ar ionization ratio is also shown in Fig. 2. This is an interesting experimental case since N_2 and F_2 have singlet electronic ground states and similar IPs, but F_2 differs from N_2 in that it has an antisymmetric rather than symmetric configuration. Accordingly, the electron interference model [15] predicts that ionization of F_2 should be suppressed by 2 orders of magnitude relative to N_2 . As shown in Fig. 2, the ionization rate of F_2 is slightly enhanced with respect to Ar . Therefore, considering our N_2 : Ar determination, the F_2 : N_2 ratio varies between 0.5 and 1.0 over the range of intensities studied.

Another interesting test case, in the context of the electron interference model [15], is S_2 . The S_2 : Xe ionization ratio is shown in Fig. 1. Like O_2 , S_2 has an antisymmetric, triplet electronic ground state. The 9.26 eV IP for S_2 differs significantly from the 12.13 eV IP of Xe . According to the simplest atomic multiphoton or tunneling models, the 2.9 eV IP difference between the two species should lead to a highly intensity dependent ionization ratio. For intensities well below saturation in either species, our tunneling calculations predict an S_2 : Xe ratio that varies from 2200 to 5 over the range of intensities shown. Clearly, our measurement of a near unit ratio of ionization probabilities indicates a significant suppression of the S_2 yield.

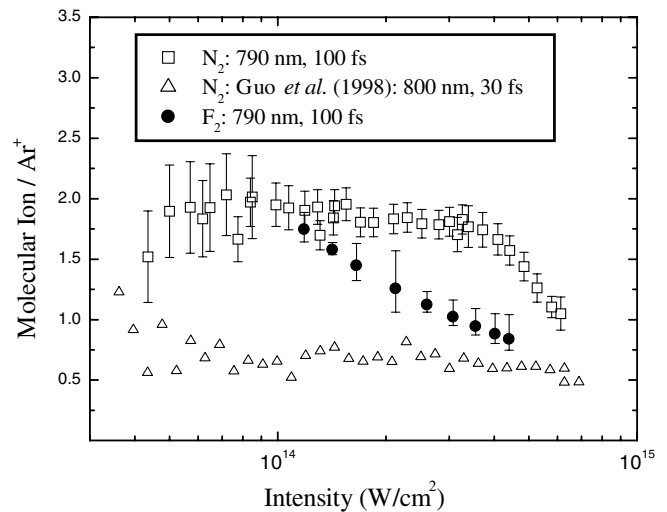


FIG. 2. The ratios of N_2^+ (IP = 15.58 eV) and F_2^+ (IP = 15.69 eV) to Ar^+ (IP = 15.76 eV) as a function of laser intensity. Over the intensity range shown, the N_2^+ , F_2^+ , and Ar^+ ionization yields vary by factors of 1×10^6 , 1200, and 1×10^6 , respectively. Clearly, the predicted [15] suppression, by 2 orders of magnitude, of F_2 ionization relative to N_2 ionization is not observed.

We note that the two molecular species that show pronounced ionization suppression have antisymmetric, triplet ground states with relatively low IP. For 790 nm radiation, significant ionization of these molecules occurs at intensities well below those where tunneling theory is strictly valid. Therefore, one might conclude that ionization suppression in molecules is a multiphoton rather than tunneling phenomenon. To test this hypothesis, S_2 ionization measurements have also been performed at 1360 nm, extending the range of experimental investigation into a regime where tunnel ionization is expected to dominate. The 80 fs, 1360 nm, 150 μJ pulses used in the experiment are created by a 790 nm pumped, optical parametric amplifier (OPA). Over virtually the entire range of intensities studied, and at both wavelengths, molecular ionization is strongly suppressed, with an ion yield ratio $0.5 < S_2^+$: Xe^+ < 3.5 .

In the electron interference model [15], ionization of diatomic molecules is complicated by interference between electrons emitted from the vicinity of individual nuclei. Ionization suppression occurs when primarily low-energy electrons are emitted with a relative π phase shift. The model calculations are in good agreement with ionization measurements of O_2 vs Xe . Furthermore, the small ionization enhancement that we observe for N_2 relative to Ar is predicted by the model [15]. Moreover, recent above-threshold ionization (ATI) measurements [20] are consistent with the predicted suppression of low energy ATI electron emission during intense-laser ionization of O_2 . However, the model also predicts strong suppression of ionization of F_2 relative to N_2 which is not observed. Also, according to the interference mechanism, ionization

suppression in S_2 should be less pronounced (compared to O_2) due to the greater internuclear separation of S_2 (1.89 a.u.) as compared to O_2 (1.21 a.u.). This increased distance reduces, by a factor of 2.4, the range of electron energies for which complete destructive interference occurs. Although no direct atomic partner is available for comparison, the S_2 :Xe ratio indicates suppression that is at least as severe as in O_2 . This observation appears to be at odds with the interference model. Apparently, the interference model does not accurately describe molecular ionization of F_2 or S_2 , or the suppression of high energy electrons in the O_2^+ spectrum [20].

In the recently proposed charge screening model [14], suppression of ionization is due to an electronic structure effect that causes an ionizing electron to see an effective nuclear charge >1 as it leaves the molecule. In the case of N_2 , it is argued that outer electrons are uniformly distributed around the core, resulting in an effective core charge of 1.0 [14], and therefore, no ionization enhancement or suppression is predicted for N_2 . This is roughly consistent with our observations. However, it seems that the model should predict suppressed ionization of F_2 which, like O_2 , has an antisymmetric wave function. This is at odds with our observations.

According to both multiphoton and tunneling models, atomic and molecular systems with nearly identical IPs should have very similar intensity-dependent ionization yields and constant ionization ratios near unity. Conversely, systems with dissimilar IPs should have ion yield ratios that continuously vary with intensity. We find, between the limits of threshold ionization and saturation, that the ratio of ion yields are roughly constant for pairs of analytes with both similar IPs and dissimilar IPs, even when these ratios are not unity. This trend continues for heteronuclear molecules (CO, NO, and SO) [18]. While the gross intensity-dependent features of the ionization probability curves of atoms and diatomic molecules are predicted using multiphoton or tunneling theories [6,7], in general, neither these models nor their more recent extensions [11–15], quantitatively describe the detailed differences between atomic and molecular ionization in most cases.

In summary, our ratiometric method provides a more precise comparison of the relative ionization rates of molecules and companion atoms than was previously available. Our ionization measurements of O_2 relative to Xe are in very good agreement with previous experimental [10] and theoretical [14,15] results. Our determination of the N_2 :Ar ionization ratio agrees with theory [15], but differs from other measurements [10,16,20] by a non-negligible factor. This discrepancy may be evidence of a pulse duration dependent dynamic effect that appears to be predicted by theory [15]. However, the measured F_2 :Ar and S_2 :Xe ratios, reported here for the first time, are at odds with theory [14,15]. Apparently, the inclusion of electronic structure-dependent core-charge screening

and/or “which path” interference in the ionizing electron waves, is insufficient to quantitatively predict ionization of these systems and, therefore, of diatomics in general.

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