Orientational averaging in the intense field tunnel ionization of molecules

Merrick J. DeWitt, Bradley S. Prall, and Robert J. Levis
Department of Chemistry, Wayne State University, Detroit, Michigan 48202

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The effect of molecular structure and orientation on the rate of tunnel ionization in intense laser fields is considered for linear molecules. The nonspherical nature of the molecular electrostatic potential near the classical electron turning point results in a nonisotropic distribution of tunneling rates. This must be considered when determining the overall ionization rate of a randomly oriented ensemble. Calculations are performed for two atom:molecule test pairs with similar ionization potential, Ar:N₂ and Xe:O₂, and the results are compared to experiments [Talebpour, Chien, and Chin, J. Phys. B 29, L677 (1996); Guo et al., Phys. Rev. A 58, R4271 (1998)]. © 2000 American Institute of Physics. [S0021-9606(00)00322-6]

INTRODUCTION

The behavior of large polyatomic systems under the influence of extremely intense lasers is much more complicated than the behavior not only of atoms, but also of small strongly bound molecules. The ability of molecules to respond to excitation through nonelectronic modes and for energy deposited though electronic excitation to be redistributed into nonelectronic modes significantly complicates the motion of molecules on their multi-dimensional potential surfaces as well as the mechanisms for moving between these surfaces. Describing molecular ionization with the zero-range potential assumed for atomic ionization therefore becomes less reasonable as the number of atoms in the molecule increases, leading to an increase in the number of available pathways for excitation and relaxation through nonelectronic modes. However, the time scales for vibrational energy redistribution are limited to the time scales of vibrational motion (i.e., maximum rates for the redistribution of internal energy are limited to approximately one vibrational quantum per vibrational period). In most molecules this limits the redistribution of vibrational energy to one or two vibrational quanta per 100 fs. In cases where the excitation and ionization time scales are limited to 100 fs, redistribution of energy through rovibronic relaxation can therefore be expected to be limited to a few vibrational quanta and the ionization event becomes increasingly electronic in character: i.e., more atomlike.

Another justification for the more atomlike ionization of molecules in the short pulse limit can be inferred from the fact that under ultrashort pulse conditions electrons can respond to the changing conditions of the field and nuclei cannot. Under these conditions the rovibronic character of the molecule is not expected to be unimportant in the excitation process, but indeed can serve as an avenue through which rigid electronic selection rules may be relaxed. This can be seen in the presence of vibronically allowed transitions (e.g., the 1A²g−1A¹g transition in formaldehyde and the B₁g−1A¹g transition in benzene) which are rigorously disallowed electronically. The understanding of short-pulse, high-intensity ionization of molecules therefore becomes a problem of understanding which molecular properties significantly effect the interaction with the field and which do not. The delocalization of electronic charge, which is at the heart of atom–atom bonding in molecules, may lead to the only important differences between ultrafast atom–field and molecule-field interactions. This delocalization effects the energy of the electron, the spatial extent of the electron, the polarizability of the electron charge density, and (in heteronuclear molecules) the dipole moment. All of these electronic properties must of course contribute to field-molecule interactions. The remaining molecular properties, vibrational and rotational degrees of freedom, should have minimal effects on this time scale, as previously noted. In light of these arguments, the model we have previously developed to extend the accepted atomic tunneling models to molecular systems is well justified. This model is inherently one-dimensional in nature, and accounts for the electronic energy and electronic delocalization of the molecules. This model has not yet been extended to account for induced and permanent multipoles. However, atoms and homodiatoms have no permanent dipoles, either globally or locally, and therefore represent cases in which the only significant effect not yet considered is the case of induced dipoles. Multipolar effects are assumed to have minor significance in the overall ionization event, even in the region of 10¹⁴ W cm⁻², as discussed subsequently.

Determination of experimental ionization rates for molecules present significant challenges the experimentalist. Considerable difficulties arise while attempting to characterize and measure beams and accurately determine analyte concentrations in the beam path making repeatability and comparison difficult. Experimental observations of the ionization rates of Ar:N₂ (Ref. 5) and Xe:O₂ (Refs. 5 and 6) are known to disagree with predictions of the most commonly accepted theories for ionization in intense fields developed by Perelomov, Popov, and Terent’ev (PPT) and Ammosov, Delone, and Krainov (ADK). These are inherently one-dimensional models which extend the pioneering work of Keldysh. The only significant atomic or molecular property which appears in these equations is the ionization potential. Since the ionization potentials of Ar and N₂ are very similar,
as well as the ionization potentials of Xe and O₂ (Table I), PPT and ADK predict that each of these pairs of systems will have similar ionization probabilities. The PPT and ADK theories also account for the angular momentum of the system, but since this is zero for the neutral ground states of Ar, Xe, N₂, and O₂, this does not effect the predicted ionization rates. Since the structure-based model includes the effects of electron delocalization in the predicted ionization behavior, these systems provide an interesting test of the model’s ability to predict the dissimilar ionization behaviors. The structural simplicity of these systems also allows a systematic extension of the one-dimensional structure-based model to a pseudo-three-dimensional model through orientational averaging.

For the theorist, performing detailed calculations on anything other than the ground state of simple molecules is difficult in the field-free case. The presence of perturbing fields approaching and exceeding the fields binding electrons to the molecules in question only complicates the calculation further. The added computational expense of managing the multi-dimensional time-dependent algorithms necessary for the multiple nuclei and multiple electrons of molecules effectively means that solutions for any molecule larger than H₂ are nearly intractable. In light of these difficulties, a time-independent, pseudo-three-dimensional tunneling model is presented. This model is an extension of the previously described one-dimensional structure-based model which has been extended to three dimensions through orientational averaging. The model is tested against the previously described experimental measurements of Ar:N₂ and Xe:O₂.

### THEORY

Tunneling calculations performed for argon and xenon were assumed to be well-approximated by simple one-dimensional tunneling calculations based upon the Wentzel–Kramers–Brillouin theory. We have described such calculations in detail previously. Tunneling calculations performed for the nitrogen and oxygen diatoms were three-dimensional calculations determined by statistically weighted orientational averaging of individual one-dimensional calculations analogous to those performed for the atoms. The tunneling rates were determined for orientations ranging from 0 degrees (along the internuclear axis) to 90 degrees (perpendicular to the internuclear axis). These rates were then scaled to determine their relative contributions to the overall three-dimensional tunneling rate.

The orientationally averaged calculation for the diatoms begins with a determination of a two-dimensional electrostatic potential. This potential is derived from the ion in the Born–Oppenheimer limit. A complication exists for calculations of the nonclosed shell ions considered, both molecular and atomic. In the cases of hydrogen, helium, and other s-shell atoms, the ion residue has no angular momentum and both the derived potential and electron density are rigorously spherical. However, when removing a p-shell electron from argon, for instance, the propensity of quantum mechanical packages to resolve pure quantum states results in the remaining electrons exhibiting angular momentum.

### TABLE I

A comparison of various properties of Ar, N₂, Xe, and O₂ and the calculated relative ionization probabilities. The orientational averaging method predicts a suppression of the ionization rate for N₂ and O₂ with respect to predictions of the ADK model. This suppression represents a minor correction to the predicted rate of N₂ ionization relative to Ar and an improvement in the predicted suppression of O₂ ionization with respect to Xe.

<table>
<thead>
<tr>
<th></th>
<th>Argon</th>
<th>Nitrogen</th>
<th>Xenon</th>
<th>Oxygen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Ar)</td>
<td>(N₂)</td>
<td>(Xe)</td>
<td>(O₂)</td>
</tr>
<tr>
<td>Vertical ionization potential (eV)</td>
<td>15.759</td>
<td>15.581</td>
<td>12.12987</td>
<td>12.30</td>
</tr>
<tr>
<td>Characteristic length (Bohr) [aligned parallel to beam]</td>
<td>4.30</td>
<td>5.55</td>
<td>5.48</td>
<td>5.99</td>
</tr>
<tr>
<td>Characteristic length (Bohr) [aligned perpendicular to beam]</td>
<td>3.49</td>
<td>4.35</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average static polarizability (Bohr³) [along bond axis]</td>
<td>11.075</td>
<td>11.744</td>
<td>27.29</td>
<td>10.670</td>
</tr>
<tr>
<td>Static polarizability (Bohr³) [perpendicular to bond axis]</td>
<td>17.616</td>
<td>16.006</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated ionization probability [normalized to Argon, 10¹⁴ W cm⁻²]</td>
<td>1</td>
<td>1.29</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental ionization probability [normalized to Argon, 10¹⁴ W cm⁻²]</td>
<td>1</td>
<td>0.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADK ionization probability [normalized to Argon, 10¹⁴ W cm⁻²]</td>
<td>1</td>
<td>1.33</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calculated ionization probability [normalized to Xenon, 10¹⁴ W cm⁻²]</td>
<td>1</td>
<td>0.67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Experimental ionization probability [normalized to Xenon, 10¹⁴ W cm⁻²]</td>
<td>1</td>
<td>0.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADK ionization probability [normalized to Xenon, 10¹⁴ W cm⁻²]</td>
<td>1</td>
<td>0.78</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
This angular momentum leads to anisotropy in the potential for these ions, and therefore in the potential seen by the single active electron of the neutral, which forms the basis of the calculation for both atoms and molecules. A similar problem exists for the oxygen molecule, where removing one electron results in symmetry breaking of the $x$- and $y$-axes, and therefore removing the rigorously cylindrical symmetry of the system. These symmetries were restored by alternately removing the electron from each of the degenerate orbitals of the system. These symmetries were restored by alternately removing the rigorously cylindrical symmetry of the system.

In order to account for the full three-dimensional nature of the field-molecule event, the one-dimensional model has been extended through orientational averaging. For molecules of arbitrary size and shape this might be accomplished via Monte Carlo methods. For molecules with high symmetry the problem can be approached by more direct methods. Diatoms (e.g., $O_2$ and $N_2$) exhibit cylindrical symmetry, and are therefore two-dimensional in nature. We determined a series of ionization rates for each molecule as a function of the angle, $\theta$, between the field vector of the laser and the bond axis. The isopotential surfaces were calculated via $ab$ initio methods. Oxygen isopotentials are shown in Fig. 1(a) and nitrogen isopotentials in Fig. 2(a). For these systems, the characteristic length, $a$, is defined as the distance between outer classical turning points in the electrostatic potential along a line parallel to the field vector and passing through the bond center. The angular dependence of the characteristic length was determined from the isopotentials, and is shown in Fig. 1(b) for oxygen and Fig. 2(b) for nitrogen. Angle dependent ionization rates were determined via a modification of the Wentzel–Kramers–Brillouin tunneling theory:

$$W = \frac{2[2IP - aF]^{3/2}}{3F},$$  

$$\text{rate} = e^{-W},$$  

where IP is the ionization potential, $a$ is the characteristic length, and $F$ is the field strength, all in atomic units. Averaging over $\theta$ results in a pseudo-two-dimensional tunneling rate derived from individual one-dimensional rates. However, there are many unique orientations of the molecule in the field which can result in a bond-field angle of $\theta$, and these must be properly counted in order to determine the proper contribution that each $\theta$-dependent ionization rate makes to the pseudo-three-dimensionally averaged tunneling rate. The total contribution of a specific angle is equivalent to the area that the field axis sweeps out on a reference sphere when rotated about the bond axis, as depicted in Fig. 3. This differential area element of the product of the circumference of the circle determined on the sphere’s surface ($2\pi \sin \theta$) and the differential width ($\Delta \theta$). The area itself is then:

$$\text{Area} = \int_{\theta-\Delta\theta/2}^{\theta+\Delta\theta/2} 2\pi \sin \theta \, d\theta$$

$$= 2\pi [\cos(\theta - \Delta\theta/2) - \cos(\theta + \Delta\theta/2)].$$

This area represents the $\theta$-dependent weighting factor for the average. However, care must be taken to ensure that the sum of the $\theta$-dependent weighting factors over the total angular range is identically one (which is not the case as shown), and corrected for this. The final orientationally averaged tunneling rate is:

$$W = \sum_{\theta=0}^{\pi/2} A_{\theta} W_{\theta},$$

where $W_{\theta}$ is the tunneling rate for the molecule whose bond axis forms an angle $\theta$ with the field vector and $A_{\theta}$ is the normalized weighting factor for angle $\theta$.

**RESULTS**

The predicted ionization rates for Ar:$N_2$ and Xe:$O_2$ are shown in Figs. 4 and 5, respectively. Calculations of the ionization rate as predicted by the ADK tunneling model were also performed for Ar:$N_2$ and Xe:$O_2$. At $10^{14}$ W cm$^{-2}$, the relative ionization rates for Ar:$N_2$ were found to be 1:1.33 for the ADK model and 1:1.29 for the orientationally
averaged model. The relative ionization rates for Xe:O₂ were found to be 1:0.78 for the ADK model and 1:0.67 for the three-dimensional model. Recent experiments⁵,⁶ have demonstrated that the relative ionization probabilities for Xe:O₂ at this intensity are approximately 1:0.1. Guo et al.⁵ also determined the Ar:N₂ ratio at this intensity to be approximately 1:0.6. The predicted ionization rates for O₂ and N₂ via both the ADK and three-dimensional model are therefore shown to be higher than the experimental observation. However, the three-dimensional model does represent a correction to the predicted rates with respect to ADK, supporting the need to consider orientational averaging in the problem of tunneling of polyatomic molecules in intense fields.

**DISCUSSION**

The orientationally averaged model, as compared to the ADK model, predicts subtle but important differences in the relative ionization rates for the systems considered. ADK, as an atomic model, produces ionization rates which are strongly a function of the ionization potential. Electronic angular momentum also plays an important role in the total ionization rate. However, the neutral ground states of each of the systems (Ar, Xe, N₂, and O₂) have the same electronic angular momentum (l=0 for the atoms and Λ=0 for the molecules), so that for a given field strength the ADK rate is a function of the ionization potential alone. In this case, the ionization rates of Ar:N₂ are expected to be nearly identical, as well as the ionization rates of Xe:O₂. Recent experiments⁵,⁶ have shown that the observed ionization rate for N₂ is suppressed with respect to Ar and that the observed ionization rate of O₂ is significantly suppressed with respect to Xe. The results of the pseudo-three-dimensional tunneling model show that orientational effects contribute to the observed depression of ionization rates for the diatoms. One assumption in any orientation averaging scheme is that the ionization times for various orientations are not so short that
saturation is occurring in all channels. In the case of the molecule O2, we find that the rate for ionization is 0.156 fs⁻¹ at 10¹⁴ W cm⁻² for molecules aligned with the laser electric field and 0.0425 fs⁻¹ for perpendicular alignment. This suggests that orientation effects are important because the molecules aligned perpendicular to the laser polarization axis have a half life of 16.2 fs. This time is on the order of the 30 fs pulse duration employed in the experimental measurements.

The effects of induced polarizability on the tunneling rate are uncertain. To a first order approximation, the ability of the system to deform in the field allows the system to stabilize itself in the field, and therefore lower its ionization rate with respect to an otherwise similar system with lower polarizability. The average static polarizabilities of argon and N₂ are 11.075 and 11.744 Bohr³, respectively. Guo et al.⁵ have suggested that the higher polarizability of N₂ therefore explains its lower ionization rate with respect to argon. However, they have shown that the polarizabilities of xenon and O₂ are 27.29 and 10.670 Bohr³ and that this would suggest a depressed ionization rate of xenon with respect to O₂, which is contrary to the experimental evidence. This seems to suggest that the polarizability is having little effect on the ionization rate. If orientational averaging has an important effect on the overall ionization rate, then the orientational dependence of polarizability should also be considered. The perpendicular and parallel components of polarizability for N₂ and O₂ are listed in Table I. For the case of Ar:N₂ the ionization rates for molecules aligned with the field would be reduced, while the rates for molecules aligned against the field would be enhanced. It is difficult to quantitatively assess what effect this would have on the overall ionization rate of N₂, but qualitatively the effects would be expected to cancel, resulting in little change in the predicted rates. For Xe:O₂, both aligned and perpendicular ionization rates of O₂ are still predicted to be enhanced with respect to the xenon rate due to the fact that both the parallel and perpendicular polarizability components of O₂ are lower than the polarizability of Xe. Again, it is difficult to determine what effect this would have quantitatively upon the overall tunneling rate, but qualitatively the rate of O₂ with respect to Xe must be enhanced. Both the N₂ and O₂ orientational considerations therefore lead again to the conclusion that the polarizability effect is probably small.

Field-induced polarization may have an effect on the ionization rate if substantial alignment occurs on the time scale of the excitation laser pulse duration. Bandrauk and Ruel¹¹ have considered the alignment of H²⁺ in a 1064 nm pulse having intensity of 10¹⁴ W cm⁻². In this work a classical expression for relative alignment time was provided based on the polarization anisotropy in a given molecule. The alignment time, τ, was found to scale as:

\[
\tau \propto \left( \frac{I}{\alpha} \right)^{1/2} \frac{E_0}{\nu},
\]

where \( I \) is the moment of inertia, and \( \alpha \) is the polarizability anisotropy. Calculations suggested that the alignment time for H²⁺ at 10¹⁴ W cm⁻² ranged from 80 to 30 fs for initial angles from 89 to 45 degrees, respectively. We estimate the time scale for alignment of O₂(N₂) is a factor of 3.69 (2.93) higher than that calculated for H²⁺, or from 295 to 110 fs given the ratio of moments of inertia, ~42 (30), and anisotropic polarizabilities, 3.23 (3.55). Given the fact that the experimental measurements employed a 30 fs duration laser beam, we conclude that limited alignment occurs in the laser intensity regime under consideration.

CONCLUSIONS

Extending previously developed one-dimensional, structure-based tunneling models for atoms and molecules to all three spatial dimensions has successfully improved the predictive ability of the structure-based model. The current ionization model contributes to the understanding of the very complicated ionization behavior of many-electron atoms and molecules which, as the experimental data suggest, are poorly understood. The orientational dependence of the ionization rate was shown to significantly effect the predicted ionization rate of O₂, and will have an even greater effect upon the predicted ionization rates of molecules with more highly anisotropic electron distributions. In light of this understanding, any arguments concerning the effects of polarizability on the overall ionization rate must also consider the orientational dependence of molecular polarizability. As in previous studies, polarizabilities cannot be shown to account for the ionization behavior, and the polarizability of the systems is therefore assumed to have little effect on the ionization event.
ACKNOWLEDGMENTS

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10 D. Bohm, Quantum Theory (Prentice Hall, New York, 1951).