

Photodissociation Dynamics of F₂ in Solid Kr: Theory versus Experiment

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(Received 1 October 1990)

Molecular-dynamics simulations were used to calculate the photodissociation yield of F₂ in solid Kr as a function of photon energy at 12 K. The calculations used pairwise interactions including empirical gas-phase F(²P_{3/2})/Kr potentials. Excellent agreement was found with recent experimental data, showing the quantitative accuracy of molecular-dynamics simulations using pairwise reagent/solvent potentials, in describing a chemical condensed-matter reaction.

PACS numbers: 31.70.-f, 33.80.Gj, 61.80.Lj

Molecular-dynamics (MD) simulations have become in recent years one of the most important tools in exploring chemical reaction dynamics in condensed media, both in liquid solutions¹ and in the solid state.² In this light it appears essential to rigorously examine the reliability and limitations of the method. In some systems, quantum effects such as tunneling are obviously important.³ However, the main concern in most cases is whether the accuracy of available interaction potentials suffices for the description of chemical reaction dynamics in condensed matter. For instance, nearly all MD studies of reactions use pairwise potentials only for the interactions between guest and host molecules, and it is unclear whether neglecting nonpairwise interactions can be justified in such treatments. Also, the adequacy of presently available pair potentials is questionable, especially for photochemical processes in which excited states are involved.

The purpose of the present study is to test the predictive power of MD simulations against experiment for a simple, prototypical photochemical reaction in condensed matter; namely, the photodissociation of molecular F₂ in crystalline krypton. As obvious from the above comments, we test mainly the suitability of the state-of-the-art interaction potentials for such processes, using exclusively pair potentials for the description of interactions between the reacting species and solvent atoms. Reactions of molecules in rare-gas solids are an optimal framework for such comparisons, since the interactions among the solvent atoms are well understood, and the reagent/solvent interactions are accurately known from gas-phase data. Photolysis of small molecules in rare-gas solids was intensively pursued in recent years, both experimentally, e.g., Refs. 4–8, and theoretically, Refs. 2 and 9. However, a quantitative comparison between experiments and MD simulations has not been reported as yet. The present Letter aims at providing such a comparison for the photolysis of F₂ in solid Kr at 12 K. Excitation of F₂ in the gas phase into its first electronic continuum results in direct separation of the photofragments

due to the repulsive nature of the excited ¹Π_u potential. When the same excitation is carried out in a rare-gas host, the cage effect due to the surrounding solvent atoms may prevent, for part of the photoabsorption events, the subsequent separation of the F atoms, resulting eventually in the recombination of the latter in the original solvent cage in which the process had begun.

Experimentally, the yield for separation of the F atoms upon photoexcitation of the F₂ was measured as a function of the excess energy (energy above the gas-phase dissociation limit of the molecule).⁷ The experiment determines the fraction of F₂ molecules which were “permanently” dissociated under the experimental conditions. The details of the experiment are described elsewhere.^{7,8} To model the process, our MD simulation approach proceeded as follows. Using available Kr/Kr potentials, and an F₂/Kr potential constructed as the sum of F/Kr interactions, classical trajectories were computed for a slab of the solid. A cubic slab of 365 atoms was used, holding the edge atoms stationary. Molecular F₂ was introduced in the center of the slab as a substitutional impurity. Previous simulations showed such a sample is large enough to eliminate finite-size effects.⁹ The trajectories of the particles were pursued until equilibration was established, with velocity distribution compatible with the 12-K temperature. The simulations show large-amplitude motions of the F₂ within the surrounding cage, the mean position of the molecular center of mass being at the substitutional site of the Kr fcc lattice. At random points in time photoexcitation is modeled to occur by switching the F-F interaction to that of the (repulsive) excited-state potential. In the spirit of the Franck-Condon principle, the positions and momenta of the lattice atoms are retained at such a jump. The trajectories of the atoms are pursued with these initial conditions and with the excited-state potentials, over a time scale of 8 ps, at which time the atoms have reached thermal equilibrium. If the two F atoms have still remained in the same cage (mutual separation of < 4 Å), we assume they will eventually recombine. Tra-

jectories where one F atom or both atoms leave the cage and wind up in different unit cells from each other count as dissociation events. It is possible, in principle, that some slow-time-scale events, not seen in the 8-ps dynamics, may lead to recombination, and thus contribute to a deviation from the measured “permanent” dissociation yield. We estimate that such processes are unlikely to be of quantitative significance at the temperature used. A set of 100 trajectories was used to calculate the photodissociation yield at each excess energy. The calculations show that the orientation of the F_2 molecule within the cage is the most important aspect of the initial-state sampling in determining whether the corresponding trajectory will lead to dissociation or to recombination.⁹

For the interactions in the excited state, we used accurate pairwise additive Kr/Kr, $F(^2P_{3/2})/Kr$, and $F(^2P_{3/2})/F(^2P_{3/2})$ potentials, all taken from gas-phase data. The interaction between an $F(^2P_{3/2})$ atom and a Kr atom involves a (ground-state) $X_{1/2}$ potential, and an excited $I_{3/2}$ potential (the two curves coalesce as the F-Kr distance becomes large), and a nonadiabatic coupling between the two states. We carried out calculations using two different models with regard to the treatment of the $F(^2P_{3/2})/Kr$ interaction: (1) The first model assumes very rapid electronic relaxation, so that only the $X_{1/2}$ potential curve is considered. We refer to this as the “one-potential” model. (2) The second is a diametrically opposite model which assumes that nonadiabatic transitions can be neglected completely, in which case the $X_{1/2}$ potential is used for half the trajectories, and the $I_{3/2}$ is used for the other half (such an equal distribution seems consistent with the initial-state preparation created by the photolysis). We refer to the second scheme as the “two-potential” model. In both approaches we neglect nonadiabatic transitions between the two electronic states throughout the process of the interatomic motion. The accurate $X_{1/2}$ and $I_{3/2}$ F-Kr potentials determined by Becker, Casavecchia, and Lee¹⁰ from molecular-beam scattering were used in the calculations.

Figure 1 shows a comparison between the experimental yield for the separation of the photofragments with the results of two sets of MD simulations; those that correspond respectively to the one-potential and to the two-potential treatment of the F-Kr interaction. The overall agreement between experiment and the theoretical calculations, especially the two-potential ones, is very good. This indicates the following: (i) *The pairwise additive reagent/solvent potentials taken from gas-phase data provide a sufficiently accurate interaction for treating the reaction dynamics in condensed matter.* The fact that nonpairwise interactions do not seem necessary is of major practical importance, if found to hold for a wide range of systems. (ii) *Classical molecular dynamics appears to be valid down to the low temperatures of the experiment (12 K).* As Fig. 1 shows the two-potential treatment is considerably better than the one-potential at low excess energies. At high excess energies both calcu-

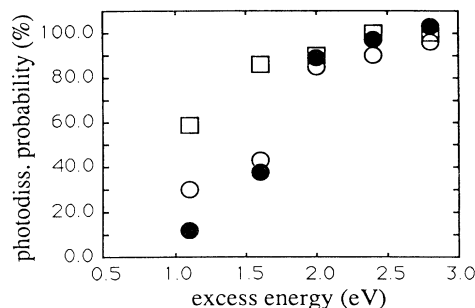


FIG. 1. Photodissociation probabilities: theory vs experiment. Theoretical simulations are based on the use of the exact F/Kr potentials (Ref. 10): open squares, one-potential model; open circles, two-potential model; solid circles, experiment (Ref. 7).

lations give excellent agreement with experiment, the single-potential treatment being perhaps slightly better (although the differences between the two are virtually within error bars). A simple interpretation is that for fragments hitting a Kr atom at moderate energies, the nonadiabatic transitions may indeed be weak; hence the two-potential treatment which preserves the initial electronic state distribution works better. At high energies the two models give similar results, but the single-potential approach may be slightly better since the nonadiabatic transition probabilities are larger, resulting in net electronic relaxation from the $I_{3/2}$ curve to the $X_{1/2}$ one.

Finally, we return to the issue of the dependence of the results upon the potential used. Having found that good pairwise reagent/solvent potentials are sufficient, we examine how sensitive the results are to the pair potentials. In Table I, we compare the results using F/Kr potentials of Becker, Casavecchia, and Lee¹⁰ with results obtained with approximate F/Kr potentials. The latter were constructed as Morse potentials, with well-depth and minimum positions that fitted those of the accurate potentials of Becker, Casavecchia, and Lee. This approach, which leads to computational efficiency, was followed by us in our previous simulations of F_2 dissociation in solid Ar.⁹ The results of Table I show that the approximate potentials give results that deviate considerably from

TABLE I. Photodissociation probabilities using the approximate and the exact potentials in the two-potential model.

Excess energy (eV)	Expt. (%)	Theory (%)	
		Approximate	Exact
1.1	12	55	30
1.6	38	65	43
2.0	89	77	85
2.4	97	85	90
2.8	100	92	96

those obtained from the "true" ones (and are in poorer agreement with experiment). Thus, *while we saw previously that accurate pairwise reagent/solvent potentials are sufficient for reliable MD calculations in this system, the sensitivity of the results to the pair potential is high, and the best pair potentials must be used.*

In the light of the above conclusion, we note that while accurate atom-atom potentials for Kr-F and Kr-Kr exist, a reliable atom-molecule potential for Kr-F₂ is not available. Such a potential is crucial for a rigorous description of the molecule-cage reorientation dynamics, which was discovered to be important in determining quantum yields of dissociation in both experiment⁷ and theory⁹ previously. Preliminary calculations at 4 K based on a KrF₂ potential constructed as a sum of atom-atom potentials indicate that the molecule remains essentially a free rotor. Therefore, the trend of inverse temperature dependence of quantum yields is smaller in this case than either experiment⁷ or prior F₂-Ar simulations⁹ would indicate. For quantitative comparisons of theory with experiment at 4 K, refinement of atom-molecule potentials and a more rigorous treatment of quantum effects (zero-point motions) are felt essential. Work along both of these lines is now in progress.

While the generality of these conclusions remains to be explored, they carry important implications on the reliability of practical MD simulations of chemical reaction dynamics in condensed matter.

This research was supported by the U.S.-Israel Binational Science Foundation (Grant No. 88-0008L to R.B.G. and V.A.A.) and by the U.S. Air Force Astronautics Laboratory (Contract No. F04611-90-K-0035). R.B.G. gratefully acknowledges support in the

framework of the Saerrer K. and Louis P. Fiedler Chair in Chemistry at the Hebrew University. The Fritz Haber Research Center is supported by the Minerva Gesellschaft for die Forschung Munich, Federal Republic of Germany. V.A.A. acknowledges financial support from the Alfred P. Sloan Foundation.

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