ENERGY TRANSFER AND DISSOCIATION IN COLLISIONS OF I$_2$ WITH MgO(100)

E. KOLODNEY, A. AMIRAV
Department of Chemistry, Tel-Aviv University, Ramat Aviv 69978, Israel

and

R. ELBER and R.B. GERBER
The Fritz Haber Center for Molecular Dynamics and The Department of Physical Chemistry,
The Hebrew University of Jerusalem, Jerusalem 91904, Israel

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Iodine molecules in supersonic beams were collided with a single crystal MgO(100) surface. The dissociation probabilities and the kinetic energies of the non-dissociated molecules were measured in the collision energy range 1–10 eV and compared with the results of classical trajectory models. Very large molecule–surface energy transfer was observed. The excellent agreement between the theoretical calculations and the experimental findings leads to detailed dynamical insight.

1. Introduction

Molecular dissociation induced by a high kinetic energy collision with a solid surface is a process of fundamental importance and interest [1–4]. We have addressed ourselves to studying both experimentally and theoretically the dissociation dynamics of a diatomic molecule striking a solid surface in order to obtain insight into the various aspects of this basic re-active gas–surface collision process. To obtain a coherent picture the following questions are being asked: (a) What is the dissociation probability per collision, and how does it vary with energy (in the 1–10 eV range)? (b) What are the angular distributions of both the scattered molecules and atoms? (c) What are the main energy transfer processes that occur in the collision? (d) How does the surface temperature affect the dissociation process? These questions are addressed in this Letter. We have chosen iodine since its large molecular weight and low dissociation energy are experimentally convenient [4].

2. Experimental

The iodine molecules were seeded in a hydrogen or helium supersonic beam, accelerated to a high kinetic energy in the range of 1–10 eV [5]. The beam was then skimmed and collimated through two differential pumping chambers into an UHV chamber (base pressure 5 × 10$^{-10}$ Torr). The accelerated beam was either square-wave modulated for phase sensitive detection or mechanically chopped for kinetic energy measurements using a time-of-flight (TOF) technique. In the UHV chamber the beam collided with a single crystal MgO(100) slab either in its (100) or (110) azimuth. The MgO surface was commercially available (Adolf–Meller). It was X-ray analyzed before mounting. The MgO surface was mounted on an UHV manipulator and annealed at about 900°C to give a highly reproducible sharp specular and first-order diffraction peaks for He and H$_2$ scattering. (A detailed study of the energy dependence of He and H$_2$ diffraction from MgO will be published elsewhere [6].) Diffraction of helium or hydrogen seeded beam was also used to determine the surface cleanliness during iodine scattering. It was found that surface temperature of $T_s \geqslant 250$°C was required.
in order to prevent iodine from covering the surface. The surface temperature was 275°C in most of the experiments. Two quadrupole mass spectrometer (QMS) heads were used for detection. One was in line with the direct molecular beam and served for kinetic energy measurements [5]. The second QMS was positioned 45° from the beam direction and mounted either 2.5 cm from the surface for high solid angle integration or 37 cm from the surface for higher angular resolution and for scattered beam TOF experiments.

3. Theoretical approach

To gain insight into the dissociation dynamics, it proved useful to carry out calculations for two different theoretical models. The first of these assumes a rigid, non-vibrating surface, thus ignoring energy transfer from the molecule to the surface. For further simplicity the surface was taken as flat. Within this model, the classical dynamics was obtained without further approximations by numerical trajectory calculations. Indeed calculations for this model system were already reported recently [3,7]. The I₂-surface interaction potential was taken as a sum of the interactions between each I atom and the surface. Each such term was taken as the repulsive potential \( V_i(z_i) = A \exp(-\alpha z_i) \), where \( z_i \) is the distance of the atom \( i \) from the surface plane. The steepness parameter \( \alpha \) was taken as 0.8 bohr\(^{-1} \) (the value of the coupling strength \( A \) does not affect the dissociation probabilities). We used the value 1.0 bohr\(^{-1} \) in previous model calculations [7] but the present value gave somewhat better agreement with the experiments. The details of the calculations, and the sampling over initial conditions (corresponding to zero vibrational and rotational energy) can be found in refs. [3,7]. The second model allows for energy transfer to the solid, in the framework of a linear-chain-type treatment of the vibrating crystal.

From the size of the I₂ molecule and the geometry of the MgO(100) surface it was estimated that the iodine strikes directly about two surface unit cells when hitting the surface: About 3 magnesium atoms and 3 oxygen atoms should, be geometry, receive the hard impact. The solid was thus replaced by a model of a chain of vibrating units, each treated as a rigid entity and taken as possessing a mass equal to that of the abovementioned group of atoms. In addition, interactions between the chain and neighbouring parallel chains were taken into account, but the latter chains were treated as static. The result is a pseudo 3D model in which I₂ collides and exchanges energy with a single chain but this chain moves in the potential of other chains. The forces between the vibrating 6-atom units were estimated as follows. The Mg-O, Mg-Mg, O-O interactions were parameterized as Morse functions, \( V_{ab}(R_{ab}) = B \{ \exp[-\beta (R_b - R_a - R_0)] - 2 \exp[-\beta (R_b - R_a - R_0)] \} \), where \( R_{ab} \) is the distance between atoms \( a \) and \( b \). We chose \( \beta = 2.0 \) bohr\(^{-1} \) in all cases, and adjusted \( B \) so as to yield the experimental Debye frequency. The \( \beta \) value used gave best agreement with the energy transfer data. \( R_0 \) is determined from crystal geometry. From the above atom-atom interactions the potentials between groups consisting of two unit cells each could be calculated. As for the interaction between I₂ and the surface, it was taken as a pairwise sum between each I atom and surface atoms (including only first-layer contributions). The interaction between an I atom and a surface atom was chosen as a repulsive exponential \( V_{1S}(R_{1S}) = A \exp(-\alpha R_{1S}) \) with a steepness parameter of \( \alpha = 0.8 \) bohr\(^{-1} \) corresponding closely to the case of the first model. A total of at least 100 vibrating units had to be included in the calculations. For much shorter chains, energy transferred to the chain was reflected at the far end of the chain and largely returned to the molecule within the collision time-scale. The results were tested with convergence with regard to the chain length used. Before the collision, the lattice taken at classical equilibrium at \( T_{\text{surface}} = 0 \) K, i.e. non-vibrating. Thus this model did not incorporate the aspect of surface temperature dependence of dissociation.

Finally, in view of the many degrees of freedom used, it was necessary for computational purposes to simplify the collision dynamics. This was done using the finding of ref. [7] that dissociation occurs in this system via the centrifugal mechanism: The molecule dissociates if it acquires sufficient rotational energy upon collision for breaking apart. Thus the vibrational degree of freedom was frozen in the calculations of the second model, and dissociation was considered to have taken place if the final angular momentum exceeded the value necessary for centrifugal breaking of the molecule. Detailed description of the model and the calculations will be published elsewhere.
4. Results and interpretation

In fig. 1 we show some experimental results demonstrating iodine dissociation and angular scattering following a single high kinetic energy (indicated in fig. 1) collision with MgO surface. The following aspects should be noted: (a) The angular scattering of I$_2$ molecules is centered near the specular reflection angle. (b) The width of the scattering angular distribution increases with increasing kinetic energy. This aspect is qualitatively different compared with iodine scattering and dissociation from sapphire [4], where the angular distribution was narrower and its width decreasing with increasing kinetic energy. (c) Molecular dissociation is evident from the substantially higher ratio of I$^-$ signal to I$_2^+$ signal at the higher kinetic energy and also from the slight asymmetry in the I$^+$ curve compared with the I$_2^+$ curve in fig. 1. The major problem in the quantification of results such as those in fig. 1 was the de-coupling of the surface induced dissociation from the electron induced dissociation in the ionizer of the QMS. If one assumes that the electron induced dissociation does not (or only slightly) depend on the iodine internal energy, then the calculations are straightforward. We have carefully checked this issue and did not find any internal energy effect on the electron induced dissociation.

The following theoretical and experimental aspects are pertinent to this problem: (a) The dissociation energy of the I$_2^+$ ion is 60.1 kcal [8] while the dissociation energy of the neutral I$_2$ molecule which is only 36.1 kcal/gnd. (b) We believe the rotational excitation to be dominant in the dissociation mechanism [5]. Rotational excitation by electron impact usually obeys ΔJ = ±1 selection rule (small deviation at 100–25 eV) [9]. (c) The dissociation probabilities extracted from measurements (assuming ionization to be independent of neutral energy) were the same within our uncertainty for different electron energies of 25, 50 and 70 eV. Most of the data were collected using reduced electron energy of 25 eV. (d) The measured angular distributions of I$_2$ were identical at 25 and 70 eV electron energy. Since we know from TOF measurements that the molecular energy loss is larger outside the specular reflection, this strongly suggests internal energy independent electron induced dissociation probability.

From the angle integrated I$^+$ and I$_2^+$ signals the dissociation probability is calculated; energy independent electron induced dissociation is assumed. This was measured when the QMS head was close (2.5 cm) to the surface for ±8° out-of-plane integration. The absolute dissociation probabilities were measured using the surface temperature effect to calibrate the QMS relative sensitivity to I$^+$ signal and I$_2^+$ signal. Raising the surface temperature resulted in reduced I$_2^+$ signal and correspondingly increased I$^+$ signal. The details of the calculation will be published in a future publication. In fig. 2 both the theoretical and experimental dissociation probabilities are plotted against the incident kinetic energy. The main features are a fast rise in the dissociation probability with a maximum rate at ≈4 eV and the dissociation probability approaching saturation at higher energy. The match between the trajectory calculation and experimental results is good. Two aspects should be noted: (a) The relative experimental probabilities are accurate within 15% but the uncertainty in the absolute value is 40% only for $P/(1 - P)$ calibrated at 4.3
Fig. 2. Molecular iodine dissociation probability on an MgO surface versus molecular iodine kinetic energy. MgO surface temperature was 275°C, nozzle diameter was 30 μm and nozzle temperature was 75°C. Both hydrogen and helium (full circles) were separately used as carrier gases. The relative uncertainty is 15%. The absolute values are uncertain within 40% calibrated at 4.8 eV using the surface temperature effect on I^ and I\textsuperscript{2}\textsuperscript{+} signals. The upper dashed curve (open circles) is the classical trajectory calculation results for the rigid surface model. The lower curve (open squares) is the trajectory calculation for a model that includes energy transfer to the solid.

The threshold is ≈2.0 eV for the calculation using a Gaussian velocity distribution with 15% width (as shown in fig. 2).

Below threshold, the experimental values for dissociation do not drop to zero probability due to a surface temperature effect which is not treated by the theoretical calculation. An important conclusion emerges when one notes the agreement in fig. 2 between the experimental dissociation probabilities and the calculations with the rigid surface model: **The dissociation probability here is almost unaffected by energy transfer to the solid.** The interpretation of the result comes from analyzing the trajectories of the more elaborate model: Dissociation follows when sufficiently high rotational excitation of the molecule is obtained upon impact [7]. For the parameters of MgO solid such rotational excitation is faster than energy transfer to solid vibrations, hence the latter can hardly affect dissociation probabilities. Note incidentally that the saturation behaviour of the probabilities is also conveniently interpreted by the centrifugal model: Only molecules having suitable orientations with respect to the surface can upon impact be rotationally excited to the point of dissociation, regardless of the collision energy.

It is important to note that there is a qualitative difference between the dissociation probabilities of I\textsubscript{2} on sapphire and on MgO\textsuperscript{+}. The dissociation probabilities of I\textsubscript{2} on sapphire could be fitted to \( P \approx k(E_K - E_D)^2 \) [4] while the dissociation probabilities on MgO are higher, with different curvature and they saturate at high energies. We have preliminary theoretical results showing that this is due to the fact that energy transfer to the solid is faster in the case of sapphire (due to stiffer vibrations, unit cell mass closer to I\textsubscript{2}, etc.). As a result, in sapphire, energy transfer to solid vibrations competes with rotational excitation, and hence also affects dissociation probabilities. Another major difference between the dissociation of I\textsubscript{2} on sapphire and MgO is the role of surface temperature. On sapphire the surface temperature in the range 100–1100°C had a negligible effect on the dissociation probabilities [4], while in MgO, in spite of the high kinetic energy and single collision conditions, it had a significant effect that will be described elsewhere. We conjecture that the physical basis for the temperature effect is the increase in dynamical corrugations associated with larger amplitudes of surface vibrations at higher temperatures. The data used in fig. 2 were taken at a surface temperature of 275°C as a compromise between the minimum surface temperature effect and a clean and unadsorbed surface as determined by He and H\textsubscript{2} diffraction. At and above 275°C surface contamination is low, and cannot be the source of the temperature dependence of dissociation. Measurements with incident velocity along the (100) and (110) directions gave similar results so that the dissociation probabilities were essentially azimuth independent.

The most important question concerning the dissociation probabilities is the energy transfer mechanism involved. We have performed an extensive study of the time-of-flight of scattered I\textsubscript{2} molecules both experimentally and theoretically, and the surprising result was that a very large amount of kinetic energy is transferred from the molecule to the surface. A typical TOF spectrum is shown in fig. 3. The narrow spectrum is the
Fig. 3. Time-of-flight spectra of $\text{I}_2$ with and without scattering from the MgO surface. The time resolution was 20 $\mu$s. The direct beam traveled 50 cm and the scattered beam traveled 25 cm to the surface and then 37 cm from it to the detector. Beam–surface angle was 22.5° which was the specular angle to the QMS at 45° to the beam direction. Surface temperature was 275°C. $\text{I}_2$ was seeded in hydrogen from a 30 $\mu$m nozzle at 75°C. Hydrogen backing pressure was 1600 Torr and the measured kinetic energies was 4.6 initial kinetic energy and 2.4 eV final kinetic energy.

direct unscattered beam and the wider and longer trace is the scattered beam at the specular angle. The direct beam traveled 25 cm to the surface and then 37 cm from it to the detector. The calculated peak kinetic energies (corrected for TOF as ions in the QMS [5]) are 4.6 and 2.4 eV. It is important to note that in spite of the large energy loss of 48% the reflected beam is definitely supersonic with a rather narrow velocity distribution. This is the main proof for the prevalence of single collisions in our experiments (in the sense that no trapping occurs). In addition we have found also that:

(a) The surface temperature has only a small effect on the amount of energy transferred to the molecules that do not dissociate, although it significantly increases the dissociation probabilities.

(b) The degree of energy loss was somewhat larger at both sides of the specular reflection.

(c) For all incident beam energies the reflection was supersonic with a small energy dependent TOF width. Our study of the $\text{I}_2$ energetics is summarized in fig. 4 where both the final kinetic energy and molecular energy loss are plotted against the initial kinetic energy.

It is seen in fig. 4 that above $\approx$5 eV the molecule loses more than 50% of its kinetic energy in a single collision! At 9.5 eV the molecule loses more than 6 eV. The final energy goes up sublinearly with the initial energy and correspondingly the energy loss increased in a supralinear way. Definitely this large energy transfer cannot be attributed to internal vibrational rotational excitation since the molecule cannot hold more than 1.6 eV rotational energy without dissociating. Electronic excitation is ruled out since we have carefully checked for light emission and found no collisionally induced fluorescence with estimated sensitivity of better than $10^{-6}$ of the collided molecules. Thus, we end up with an extremely large single collision energy transfer to the MgO surface. As fig. 4 shows, the simplistic theory using a vibrating chain model of the solid reproduces the experimental results on the energy transfer rather well. The theory shows that energy transfer from $\text{I}_2$ to MgO is very effective provided the collision takes place at an orientation angle unfavourable to rotational excitation because the latter takes up the collision energy more effectively than the MgO vibration and causes dissociation. Large energy transfer to the solid thus occurs for non-dissociating collisions only.

5. Conclusion

In this Letter experimental and theoretical results were presented on the dissociation probabilities of $\text{I}_2$
molecules striking an MgO(100) surface and on the kinetic energy loss of the non-dissociated I₂ molecules scattered from this surface. The favourable comparison between the experimental and the theoretical results leads to a coherent interpretation of the collision dynamics in the I₂/MgO(100) systems. It is concluded that the dissociation is almost unaffected by energy transfer to the surface, and this is attributed by theory to faster transfer of collision energy to the rotational mode (which leads to dissociation by the centrifugal mechanism) than to the solid.

Investigation of dissociation mechanisms in other molecule–surface systems through a combined experimental–theoretical approach seems highly desirable and should throw light on the influence of properties of the molecule and the solid upon the dissociation mechanism.

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