LABORATORY SYNTHESIS OF MOLECULAR HYDROGEN ON SURFACES OF ASTROPHYSICAL INTEREST

V. PIRRONELLO

Istituto di Fisica, Università di Catania, Catania, Sicily, Italy; and Department of Physics, Syracuse University, Syracuse, NY 13244-1130

AND

CHI LIU, LIYONG SHEN, AND GIANFRANCO VIDALI[1]

Solid State Science and Technology Program and Department of Physics, Syracuse University, Syracuse, NY 13244-1130

ABSTRACT

We report on the first results of experiments to measure the recombination rate of hydrogen on surfaces of astrophysical interest. Our measurements give lower values for the recombination efficiency (sticking probability S times the probability of recombination upon H-H encounter, γ) than model-based estimates. We propose that our results can be reconciled with *average* estimates of the recombination rate $[(1/2)n_H n_g v_H AS\gamma]$ from astronomical observations, if the actual surface of an average grain is rougher, and its area bigger, than the one considered in models.

Subject headings: dust, extinction — ISM: abundances — ISM: molecules — molecular processes

1. INTRODUCTION

H$_2$ formation in the interstellar medium (ISM) is a fundamental process in astrophysics. The radiative association of two hydrogen atoms is a process too rare to be efficient because it involves forbidden roto-vibrational transitions, and gas-phase three-body reactions are rare in the diffuse ISM to explain H$_2$ abundance. It has long been recognized that hydrogen recombination occurs on surfaces of dust grains, where the grains act as the third body in the H + H reaction (Duley & Williams 1984).

The critical physical steps in which interstellar grains act as catalysts for the H$_2$ synthesis are (1) sticking and accommodation of gas-phase atoms on the grain surface; (2) mobility of H adatoms to meet each other within their residence time on the cold grain; and (3) ejection of the newly formed molecule into the gas phase.

The efficiency of these processes depends on the structure and the chemical activity of the grain surface, whether it is silicon bearing (silicates can be not very stable in UV radiation fields; Hong & Greenberg 1980; Greenberg & Li 1996 and references therein), carbonaceous (carbon can possibly be distributed on silicon-bearing grain surfaces), or icy (Mathis 1993). In the case of more chemically active surfaces, like carbonaceous ones, the possible presence of unsaturated bonds will increase the percentage of chemisorption events. The morphology of the surface should influence the sticking and tunneling processes; it is reasonable to assume that sticking will be higher and diffusion length lower on amorphous than on crystalline surfaces. Amorphous is the most probable structure for grains in space, as shown by observations (Leger et al. 1979).

Observed H$_2$ abundance in diffuse clouds can be explained if the formation rate R on grains balances its destruction rate; the canonical value of R is $\sim 3 \times 10^{-17}$ cm^3 s^{-1} (Jura 1975); on grain surfaces, the recombination rate can be described as $\sim (1/2)n_H n_g v_H AS\gamma$, where n_H and n_g are the number densities of hydrogen atoms and dust grains, respectively, and v_H is their

relative velocity. S (the sticking coefficient) is the probability that an atom hitting a dust grain remains on the surface, and γ is the probability that an atom, once on the surface, makes an encounter with another H atom and recombines with it. For a typical diffuse cloud environment (Jura 1975) it is assumed that, on average, $S\gamma \sim 0.3$.

From a theoretical standpoint, the complexity of the problem lies in the fact that, owing to the quantum nature of the H atom, a quantum mechanical calculation has to be done on a realistic, heterogeneous surface resembling dust grains in the ISM. Hollenbach & Salpeter (1970, 1971, hereafter collectively HS) calculated S using a simple semiclassical method for the atom-surface interaction, and found S to be between 10^{-1} and 1 in most cases. Leitch-Devlin & Williams (1984, 1985) used a quantum mechanical approach and assumed a perfect single crystal with energy loss due to single phonon excitations. Their sticking coefficient increases with gas temperature, reaches a maximum at $k_B T$ comparable to phonon energies, and then decreases again. Buch & Zhang (1991) numerically evaluated the sticking of hydrogen atoms on a cluster (amorphous in structure) of water molecules. They obtained $S = (k_B T/E_0 + 1)^{-2}$, where E_0 is a parameter ($\sim 100 k_B T$ for H and $\sim 200 k_B T$ for D)

In HS's calculation (Hollenbach & Salpeter 1970, 1971), the tunneling efficiency of adsorbed hydrogen was high enough to ensure a very fast scanning of virtually all possible adsorption sites on a grain surface in a fraction of the residence time of the adsorbed species. In their model, the grain surface has two adsorption sites for H, one weak (~ 400 K) and the other strong ($\sim 20,000$ K). If only one weak adsorption site is present, H atoms would not spend enough time on the surface to meet other H atoms, and they would evaporate in a time $\tau \sim \tau_0 \exp(E/k_B T)$, where τ_0 is a typical time of a vibration of an H atom in an adsorption site.

Smoluchowski (1981, 1983) did a quantum mechanical calculation and found that H would get trapped in the deepest sites of an amorphous surface after a few hops. His efficiency of H$_2$ production is several orders of magnitude smaller than HS's. Pirronello & Averna (1988) and Averna & Pirronello (1991) investigated the possibility that H$_2$ could be produced in

dense clouds by cosmic-ray bombardment of grain mantles. Within the Smoluchowski model, they found that the cosmic-ray mechanism would be dominant over H_2 recombination on grains at 10 K.

Although sticking has been extensively studied experimentally (Rendulic 1992), it has been done in conditions and on surfaces of almost no astrophysical interest, except for the following studies: Brackmann & Fite (1961) measured a sticking probability of 0.2 on an H_2-free surface and 0.5 on top of an H_2 layer in the temperature range 2.5–8 K. Because of poor vacuum conditions of their apparatus, it is assumed that their surfaces were covered with thick cryodeposits of background gas. There have been even fewer determinations in the laboratory of the hydrogen recombination coefficient on surfaces, and up to now in conditions of no astrophysical relevancy. Schutte et al. (1976) measured the H recombination on a surface of a bolometer at 3 K, a temperature significantly smaller than the one of interstellar grains (10–15 K). They found $S\gamma \sim 0.05$–0.1 on a hypothetically H_2-free surface. Other experiments (Schermann et al. 1993; King & Wise 1963) measured recombination rates in situations where either the surface temperature or the kinetic energy of the H atoms was high. On the other hand, H-beam–scattering experiments have shown that the interaction of *low-energy* H beams with single-crystal graphite surfaces is rather weak; the ground state is ~ 32 meV deep (Ghio et al. 1980). Experiments of scattering of H from graphite single crystals above ~ 16 K gave a sticking coefficient less than 0.1 and negligibly small above 21 K (Lin & Vidali 1996).

The experimental studies mentioned above, although they gave interesting information about physical/chemical process at surfaces, did not really address the question of measuring the hydrogen recombination rate on surfaces in situations which could be related to astronomical observations. Our study attempts to address this need.

In this Letter we present the results of a set of experiments to measure the recombination coefficient on the surface of an olivine slab (a silicate rich in Fe, Mg, Si, and oxygen), an astrophysically relevant material, even if polycrystalline, as natural stones on Earth are, and not amorphous, as required by observations (Draine & Lee 1984). Low kinetic energy of H beams, low fluxes, and low surface temperature have been used.

2. EXPERIMENTAL SETUP

The experiments were performed in an ultra–high-vacuum apparatus consisting of a scattering chamber and of two triply differentially pumped beam lines (see Fig. 1). Each atomic beam is produced by radio frequency (RF) dissociation of molecular hydrogen (or deuterium) in a water-cooled Pyrex tube placed in a RF cavity. A power supply provides 100–150 W of power to the cavities via a power splitter and impedance-matching networks. By using H and D beams, the recombination product (HD) can be formed only on the surface, and not in the beam source due to imperfect dissociation, as in the case when only one beam is used. The dissociation rate is measured by the quadrupole mass spectrometer in the main chamber. The maximum dissociation rate is over 90%, but in most cases was lower, around 70%–85%, and it remained constant during experimental runs. Each beam is made by the expansion of a low-pressure gas (0.1–0.2 torr) into vacuum through a short aluminum capillary 1 mm in diameter connected to a liquid
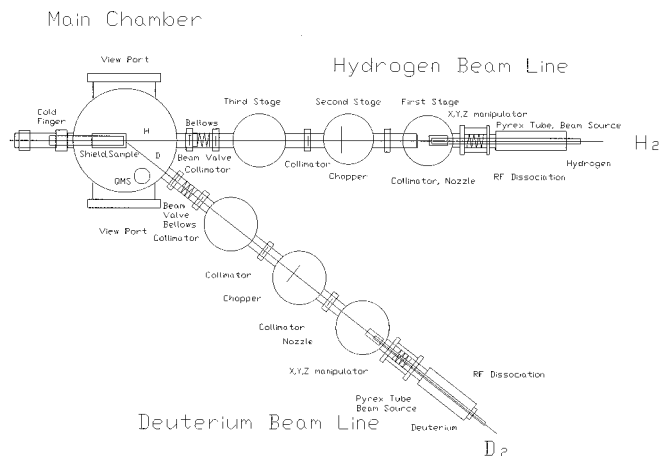

Fig. 1.—Schematic top view of the apparatus.

nitrogen (LN_2) reservoir. The beams enter the scattering chamber through 3 mm collimators. The estimated solid angle is 6×10^{-6} sr, and the flux for H is $\sim 10^{12}$ atoms cm^{-2} s^{-1}. To obtain a lower flux, a mechanical chopper with a duty cycle of 1:20 was used. The H beam hits the surface of the sample perpendicularly, while the D beam hits it at 38° from the normal. The sample is mounted on a copper sample holder that is in good thermal contact with a HeliTrans cold finger, and its temperature is measured via two calibrated chromel/iron-gold thermocouples pressed against the top and bottom surfaces of the sample. The lowest temperature reached with the cold finger is ~ 5–6 K (top thermocouple). The sample can be heated by radiation and electron-beam bombardment with a heater placed in a small cavity of the sample holder just behind the sample. The incoming and reflected beams are detected by a differentially pumped quadrupole mass spectrometer.

3. MEASURING PROCEDURES AND RESULTS

Most of the results reported here are for a sample of olivine donated by P. Plescia of the CNR Institute for the Treatment of Minerals (Rome). It consists of a mixture of Fe_2SiO_4 and Mg_2SiO_4. Prior to insertion into the apparatus, the sample was cleaned with mild solvents (acetone, methanol, freon) in an ultrasonic bath. The sample was then placed on the sample holder in the ultrahigh vacuum chamber, and the apparatus was baked at 150°C for a couple of days. The base pressure was in the mid-10^{-10} torr range. In a typical experiment, the sample is first heated to 200°C for cleaning. After cooling, it is exposed for a given amount of time to the H and D beams. During the adsorption time, the detector is placed in front of the sample and the mass is tuned to 3 (i.e., mass of HD). There is no other background gas contributing to the spectrometer signal at mass 3. At the end of the exposure time, the sample temperature is quickly (~ 1 K s^{-1}) raised to over 30 K by shutting the He flow to the tip of the cryostat; the amount of HD desorbed as a function of time is recorded into a multichannel scaler. A set of representative traces is shown in Figure 2. An analysis of desorption kinetics is given elsewhere (Vidali, Liu, & Shen 1996).

The background pressure of HD due to finite pumping capacity and/or recombination of H and D on the walls of the chamber is measured prior to and after each adsorp-
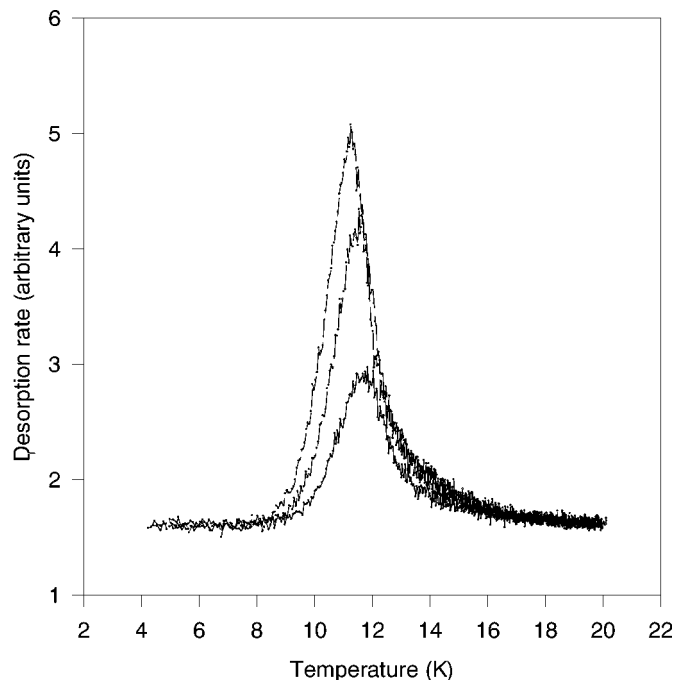
FIG. 2.—Representative thermal desorption ion curves of HD from olivine; exposure to H and D for 2, 1.5, and 1 minute (*top to bottom*) at 5 K; heating rate: ∼1 K s^{-1}.

FIG. 4.—Desorption yield of HD from olivine after adsorption of H and D at the indicated temperatures. Exposure time: 1 minute (*line:* guide to the eye).

tion/desorption experiment, in front and back of the sample, and is subtracted from the recorded signal. We checked that after the blow-off of the HD layer there is no readsorption of HD from the gas phase. The sample holder is hugged by a copper radiation shield; no adsorption/desorption of HD has been detected on or from the shield, whose temperature is considerably higher than the sample. Exposure times have been changed over several decades (see Fig. 3, where the
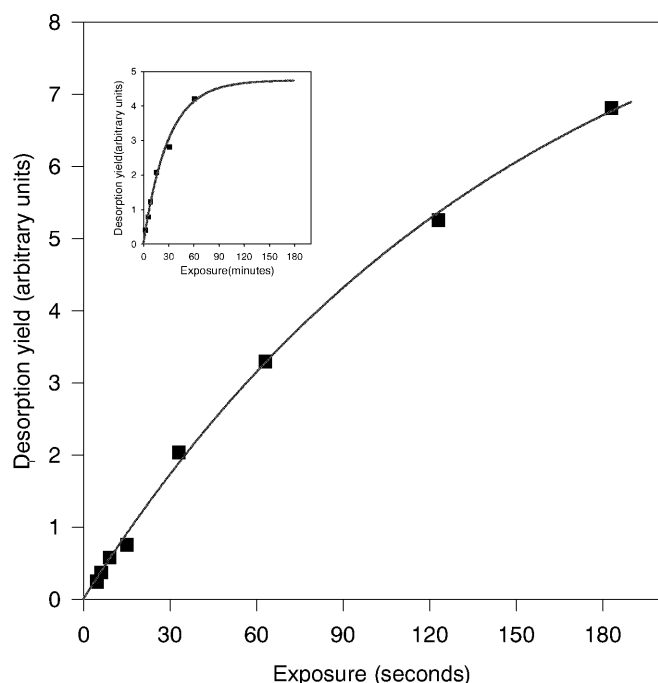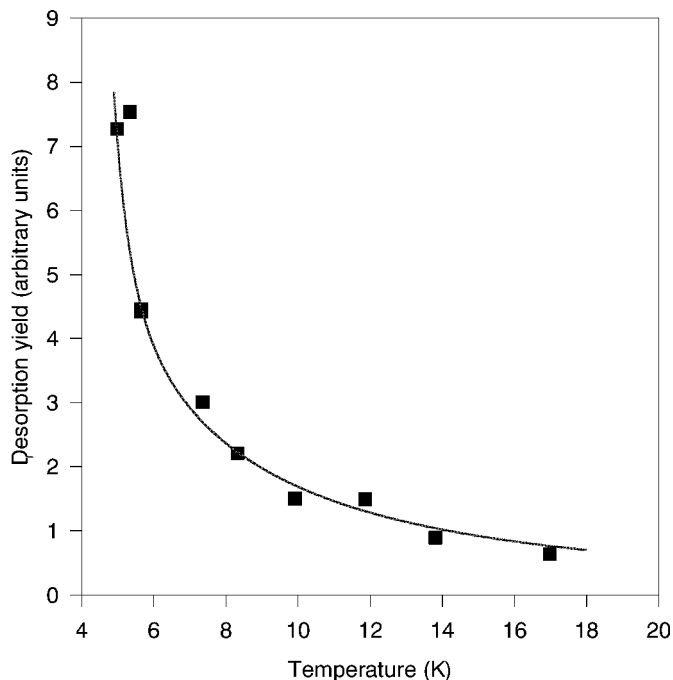

FIG. 3.—HD desorption rate from olivine vs. exposure time. Notice the different units in the abscissa in the two panels (*line:* fit; see text).

desorption yield, which is the integral of the curve in Fig. 2) is plotted against exposure to H and D. The data are fitted well by a Langmuir adsorption kinetics. The saturation of the signal is interpreted as due to the completion of the first layer. The time it takes to form an HD layer is consistent with the calculated flux and a low (∼0.1) sticking coefficient (Brackmann & Fite 1961; Schutte et al. 1976).

Figure 4 shows the amount of HD desorbed following adsorption of H and D at various sample temperatures. The amount of HD produced and released *during* the adsorption process (as measured by the mass spectrometer) is typically much smaller than the amount released in the thermal desorption run. This means that at low sample temperatures (5–7 K), H sticks (although with a sticking probability well below 1) and readily recombines; because of the low temperature, only HD that has just formed remains on the surface. At higher sample temperatures (10–15 K), H does not stay on the surface long enough to recombine, and the HD yield is much smaller. Likely, only those H atoms that became trapped in strong binding sites are retained at these temperatures; HD is then produced at reduced rates because of slow diffusion of H atoms out of these deeper energy sites. We could not measure the H signal during adsorption/desorption in a quantitative way because of the presence of a background of H in a stainless-steel system (even at 5×10^{-10} torr total base pressure). An analysis of desorption kinetics after adsorption of H at high sample temperature could yield some valuable clues; at present, however, the desorption signals are too low for a meaningful quantitative analysis.

4. DISCUSSION

The recombination efficiency of HD, here defined as the fraction of H atoms that stick and recombine to form HD, or $r \sim S\gamma$, is calculated as follows (note that this is different from the recombination rate R defined earlier): $r = (I_a + I_d)/I_{\mathrm{in}}$,
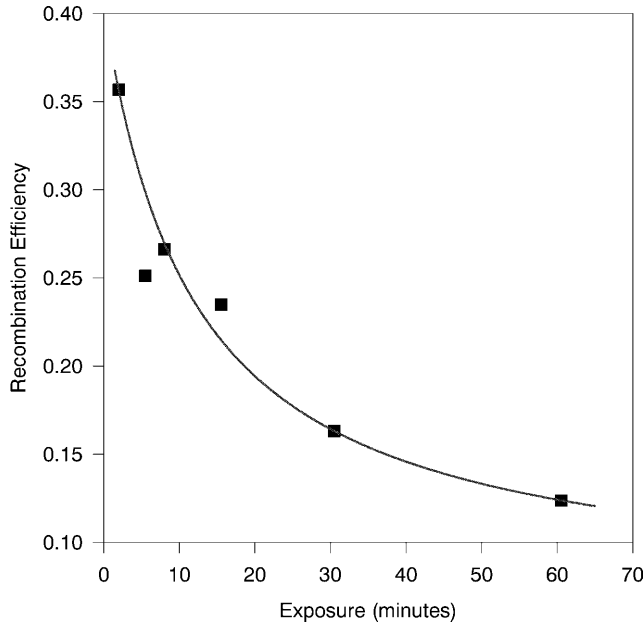
Fig. 5.—HD recombination efficiency r vs. exposure time at ~6 K (*line:* guide to the eye).

where I_a is the HD signal during adsorption, I_d is the total amount of HD desorbed after the adsorption process, and I_{in} is the amount of H sent into the chamber. The signals are corrected for velocity-dependent detection efficiency and for the measured solid angle of the detector; r is also corrected for the probability of forming HD rather than H_2 or D_2, and for the different measured intensities of the H and D beams. As mentioned before, only a small fraction of the amount of HD that desorbs in the thermal programmed desorption leaves the sample during the *adsorption process*. Consequently, the recombination efficiency drops with increasing surface temperature similarly to the falloff of the desorption yield as a function of temperature (see Fig. 4). The recombination efficiency was measured for different exposures to H and D, as seen in Figure 5.

Other candidate materials for grains in the ISM are carbonaceous solids, both amorphous and crystalline, and icy mantles (Mathis 1993). We plan to investigate the formation of molecular hydrogen also on these other materials, and we have already obtained some preliminary results (to be published elsewhere) for D_2 recombination on highly oriented pyrolitic graphite.

Our estimate of r at 5–6 K is not far from Schutte et al.'s (1976) value obtained on a uncharacterized surface of a semiconductor bolometer but at considerably lower temperature (3 K). At the astrophysically relevant grain temperature range of 10–15 K, our result, $r \sim 0.03$–0.05, is noticeably lower than the value of HS's model (Hollenbach & Salpeter 1970, 1971), ~0.3 at 10–15 K.

We might try to speculate on the reason for this difference. Calculations are for very idealized surfaces. There are a few assumptions that can influence the outcome of the calculation, such as the semiclassical description, the energetics of the binding sites, and the tunneling time between sites. The sample used by us presents a far more heterogeneous environment, both energetically and morphologically, than has been considered in theoretical models. In a real surface, tunneling might proceed much more slowly, and the sticking coefficient for H on surfaces of olivine and graphite might be much different than previously calculated on model surfaces. Considering that many models (Duley & Williams 1984) assume $S \sim 0.3$, and that a determination of S for H on graphite at ~16 K gives $S \sim 0.06$–0.1 (Lin & Vidali 1996), it is conceivable that S is only partially responsible for the fact that our $r = S\gamma$ is a factor of 10 lower than Hollenbach's, and that γ might be appreciably less than 1, contrary to what is most often assumed in models.

What are the consequences of this determination of $S\gamma$ for the recombination rate R giving the constraints posed by astronomical observations? In order to reconcile our value for $r = S\gamma \sim 0.03$–0.05 with the accepted value (Jura 1975) for $R [\sim(1$–$3) \times 10^{-17} \text{ cm}^3 \text{ s}^{-1}]$, we propose that the surface area of grains (which, in a simple model, enters the expression for $R \sim (1/2)n_H n_g v_H A S\gamma$ as a multiplicative factor) might be larger (by a factor of 5–10 or even more for amorphous surfaces). This could indeed be the case if grains have a larger surface area (i.e., they are "fluffier") (Mathis & Whiffen 1989) than previously considered. This is not an unlikely scenario, considering the type of processing that grains are subjected to in the ISM, and more theoretical and experimental effort should be devoted to verify it.

REFERENCES

Averna, D., & Pirronello, V. 1991, A&A, 245, 239
Brackmann, R. T., & Fite, W. L. 1961, J. Chem. Phys., 34, 1572
Buch, V., & Zhang, Q. 1991, ApJ, 379, 647
Draine, B. T., & Lee, H. M. 1984, ApJ, 285, 89
Duley, W. W., & Williams, D. A. 1984, Interstellar Chemistry (New York: Academic)
Ghio, E., Mattera, L., Salvo, C., Tommasini, F., & Valbusa, U. 1980, J. Chem. Phys., 73, 556
Greenberg, J. M., & Li, A. 1996, A&A, 309, 258
Hollenbach, D., & Salpeter, E. E. 1970, J. Chem. Phys., 53, 79;
———. 1971, ApJ, 163, 155
Hong, S. S., & Greenberg, J. M. 1980, A&A, 88, 194
Jura, M. 1975, ApJ, 197, 575
King, A. B., & Wise, H. 1963, J. Phys. Chem., 67, 1163
Leger, A., Klein, J., de Cheveigne, S., Guinet, C., Defourneau, D., & Belin, M. 1979, A&A, 79, 256
Leitch-Devlin, M. A., & Williams, D. A. 1984, MNRAS, 210, 577

Leitch-Devlin, M. A., & Williams, D. A. 1985, MNRAS, 213, 295
Lin, J., & G. Vidali, G. 1996, in The Cosmic Dust Connection, ed. M. Greenberg & V. Pirronello (Dordrecht: Kluwer), in press
Mathis, J. M. 1993, Rep. Prog. Phys., 56, 605
Mathis, J. S., & Whiffen, G. 1989, ApJ, 341, 808
Pirronello, V., & Averna, D. 1988, A&A, 196, 201
Rendulic, K. D. 1992, Surf. Sci., 272, 34
Schermann, C., Gough, S. F., Pichou, F., Landau, M., Hall, R. I., & Curie, M. 1993, in AIP Conf. Proc. 312, Molecules and Grains in Space, ed. I. Nenner (New York: AIP), 801
Schutte, A., Bassi, D., Tommasini, F., Turelli, F., Scoles, G., & Herman, L. J. F. 1976, J. Chem. Phys., 64, 4135
Smoluchowski, R. 1981, Ap&SS, 75, 353
———. 1983, J. Phys. Chem., 87, 4229
Vidali, G., Liu, C., & Shen, L. 1997, in Surface Diffusion: Atomistic and Collective Processes, ed. M. C. Tringides (New York: Plenum), in press