PHYSICAL REVIEW A VOLUME 54, NUMBER 4 OCTOBER 1996

Photoatomic effect: Light-induced ejection of Na and Na_2 from polydimethylsiloxane surfaces

J. H. Xu, A. Gozzini, and F. Mango
Scuola Normale Superiore, Piazza dei Cavalieri 7, I-56100, Pisa, Italy

G. Alzetta
Dipartimento di Fisica, Università di Pisa, 56100, Pisa, Italy

R. A Bernheim
Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

(Received 1 March 1996)

The photoejection of Na and Na_2 from surfaces prepared by adsorption of sodium vapor on solid films of polydimethylsiloxane (PDMS) of various molecular weights and structures is found to be dependent on light intensity and frequency. At low power levels the desorption yields of Na and Na_2 are linear functions of desorbing light power and exhibit frequency thresholds for photoejection analogous to the photoelectric effect. The frequency thresholds are 9500 cm^{-1} for Na and 11 500 cm^{-1} for Na_2, and the 2000-cm^{-1} difference can be accounted for with a model in which the alkali-metal species form charge-transfer complexes Na^+PDMS^- and $Na_2{}^+PDMS^-$, with the cations stabilized by interaction with the oxygen atoms of the PDMS polymer backbone. The ejection mechanism takes place by a reverse charge transfer to form a less polar complex with enough energy to eject Na or Na_2 from the surface. [S1050-2947(96)05510-2]

PACS number(s): 34.50.Dy, 79.20.La

I. INTRODUCTION

Recently, an unusual photodesorption phenomenon was reported for alkali-metal atoms adsorbed on polymeric films of polydimethylsiloxane (PDMS) [1]. The effect is unusual because the desorption is easily induced with very weak visible radiation, and it is characterized by a frequency threshold analogous to the work function of the photoelectric effect in metals.

Films of PDMS, as well as other substances such as high molecular weight hydrocarbons, have been used as wall coatings for optical pumping experiments on alkali-metal vapors contained in cells. They are useful because they can dramatically reduce the atomic spin relaxation that otherwise would result from wall collisions. In the case of PDMS, the polymer also adsorbs alkali-metal atoms that can subsequently be desorbed by illumination with visible radiation. This photodesorption mechanism seems to be unique for PDMS films, as it has not been detected for a variety of other coating materials such as parafins or crown ethers.

In addition to atomic desorption, alkali-metal dimers are also photodesorbed by visible radiation, but with a threshold frequency that is larger than that found for atoms. This latter observation is the object of the present contribution and with the atomic data can be used to postulate a model for the adsorption-photodesorption mechanism for alkali-metal atoms or dimers from PDMS films.

II. Na ATOMIC DESORPTION

It was shown previously [1] that the photodesorption of Na atoms from PDMS films is conveniently monitored using either absorption of atomic resonance radiation or laser-induced fluorescence (LIF). When a PDMS-coated cell, loaded with a small amount of metallic Na, is illuminated at room temperature by laser radiation tuned to either the D_1 or D_2 atomic Na resonance transition, an intense Na resonance fluorescence is observed even at incident-cw-power levels of 1 mW or less. The intensity of the Na LIF produced under these conditions at room temperature is comparable to that normally observed in an uncoated cell filled with Na vapor in equilibrium with the condensed phase at 170 °C. This observation of a strong Na LIF at room temperature is unusual enough to be quite spectacular and startling when seen for the first time. The resulting increase in the gas phase Na atom density is typically *five orders of magnitude* greater than the normal room-temperature vapor pressure of Na metal [2].

Using very weak laser power levels for a LIF probe of the vapor density in the coated cell, a significant Na fluorescence increase is produced when the darkened room is illuminated, which is one piece of evidence that the effect is not due to a simple thermal heating produced by the laser, but is induced by diffuse, weak nonresonant radiation. Using weak laser radiation to probe the increased Na vapor density produced by the photodesorption, the dependence of the desorption on the power and the frequency of the light can be separately studied using a second laser. For low light levels, the atomic desorption rate is found to be linearly dependent on the desorbing light power, but exhibits saturation behavior at high illumination powers [1]. When the desorbing laser frequency is changed, it is found that the desorption rate increases with light frequency. From this dependence, a frequency threshold for atomic desorption can be extracted. The light-induced sodium atomic desorption rate decreases with temperature but can still be observed at -90 °C. This ‘‘photoatomic’’ effect was also observed for K and Rb atoms [1] and was further studied for Rb [3].

In the present work these phenomena, already studied for Na atoms, are compared to parallel results for Na_2 molecules. An examination of the difference in threshold behav-

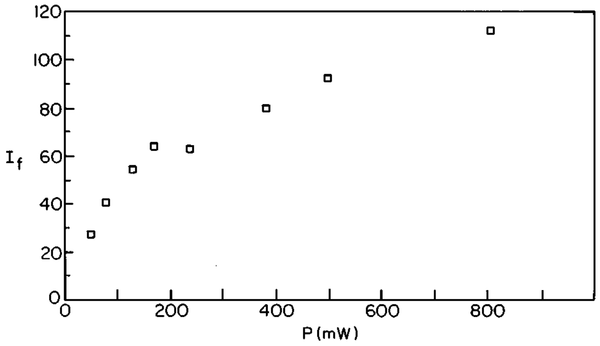


FIG. 1. Na_2 photodesorption yield in arbitrary units measured by LIF using a 30-mW laser probe at 488 nm and an additional 1-mm-diameter 488-nm desorbing laser beam applied to the cell at variable power P. The cell is at room temperature.

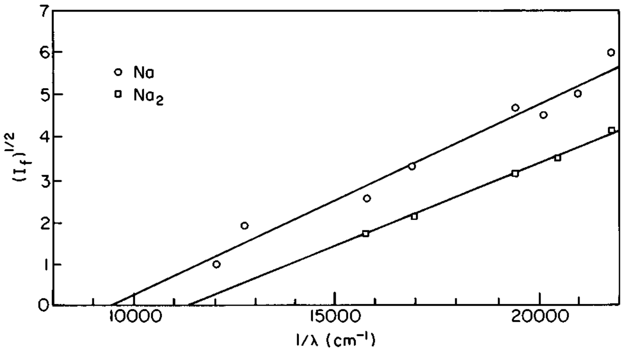


FIG. 2. The dependence of the square root of the Na and Na_2 photodesorption yields in arbitrary units, displayed as the square root of the Na and Na_2 LIF, on the frequency of the desorbing radiation. The cell is at room temperature.

ior between atoms and dimers yields evidence for the adsorbate structure and the photoejection mechanism.

III. Na_2 DIMER DESORPTION

The experimental arrangement and the cell preparation are identical to that described previously for the experiments on Na atoms [1]. A small amount of sodium metal is evaporated into glass cells that have been prepared with an interior coating of PDMS compounds or polymers. Measurement of the gas phase sodium dimer density is accomplished by means of Na_2 LIF with 488-nm radiation from an argon ion laser. The resulting Na_2 $(B^1\Pi_u - X^1\Sigma_g^+)$ LIF is dispersed with a JY1000 monochromator, and the dimer density is monitored by observing the intensity of one of the Na_2 $(B^1\Pi_u - X^1\Sigma_g^+)$ rovibrational emission transitions. The Na_2 dimer desorption rate is found to be approximately linearly dependent on the desorbing light power at low power, and a saturation behavior at high powers. This result at room temperature for Na_2 is shown in Fig. 1 for one cell preparation. While a small threshold in desorbing light power for Na_2 cannot be ruled out, the dependence of desorbed Na_2 density $[Na_2]$ on the applied laser power P is certainty not greater than $n=1$ for $[Na_2]\ \alpha\ P^n$. For atomic sodium, careful measurements showed that $n=1$ over a broad range of laser power, with no evidence for a power threshold [1]. As was discussed for Na atoms, the measured LIF intensity represents a steady state for a mechanism that includes (1) photodesorption, (2) surface adsorption from the vapor, and (3) surface diffusion into the illuminated region. As in the case for atoms, the saturation behavior at higher powers merely represents a lack of replenishment of the desorbed Na_2 species by the adsorption and surface diffusion steps in the process.

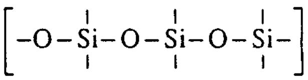
Various cw-laser lines were used to measure the dependence of the dimer photodesorption rate on frequency. For both Na and Na_2 the ejecting radiation sources were laser beams with constant power (always 30 mW) and constant illumination areas (always a 1.5-mm-diameter spot), but different frequencies. For the Na_2 photoejection measurements as a function of ejection light frequency, the Na_2 LIF was measured with 70 mW of 488-nm radiation. The increase in Na_2 LIF produced by the 30 mW of laser radiation at different frequencies was recorded and is displayed in Fig. 2 as the square root of the additional fluorescence intensity. The data for the Na atomic photoejection shown in Fig. 2 were obtained under identical conditions in separate experiments except that a weak, 1-mW-probe laser was used to obtain the Na atomic LIF. Because of the possibility of damage to the surface composition of the sodium-PDMS film, the experimental sequence in which the different frequencies were applied was varied, and the experiment was repeated several times using different positions on the glass cell for the photodesorption process. Each desorption measurement was made after sufficient time had elapsed for the desorbed Na_2 density to reach a steady state in the cell. Furthermore, each measurement was initiated only after the dimer density in the cell had returned to its normal equilibrium value in the absence of the desorbing light. All measurements were made at room temperature. With these precautions, good reproducibility was obtained for the equilibrium dimer density in the cell produced in a number of experiments by different desorption light frequencies at constant power and illumination area. Data for Na_2 were taken at five different light frequencies between 15 900 and 21 900 cm^{-1}. The reason for displaying the data as (fluorescence intensity)$^{1/2}$ vs desorption frequency is given below, where an argument is presented that this should be a linear relationship. The salient features of the plots for the square root of the Na and Na_2 production vs incident-photon energy are their linearity and the fact that both are characterized by a threshold in frequency, the threshold for sodium dimers at 11 500 cm^{-1} being 2000 cm^{-1} higher than that for sodium atoms at 9500 cm^{-1}.

At finite temperatures a sharp energy threshold for photodesorption of an atom is not to be expected. Any kind of photochemical change, whether photodissociation or photodesorption, is expected to be a function of the thermal population of energy levels of the initial state of the system. The same problem exists for the photoelectric effect where the photoelectron yield as a function of photon frequency reflects the thermal distribution of electrons around the Fermi level in the metal. For the photoelectric effect this problem was solved many years ago by Fowler [4] and DuBridge [5] who were able to extract the value of the work function that would be associated with the photoelectric effect if measured at 0 K. These considerations that have been successfully used for the photoelectric effect have an analogous applicability for the photodesorption of atoms and dimers.

IV. THE ADSORPTION-PHOTODESORPTION PROCESS

Any model that is postulated for the observed adsorption-photodesorption process must (1) contain a threshold behavior for the photodesorption yield as a function of photon frequency and (2) give a reasonable explanation as to why the threshold for Na atom photodesorption is 2000 cm^{-1} less than that for Na_2 dimers. The fact that the process can be produced by weak, visible light and that the threshold energies are less than 2 eV must also be accounted for. A reasonable interpretation of these observations is presented here.

First of all, the photodesorption of Na atoms is readily observed from a variety of different dimethylsiloxane compounds used as surface films [1] One question that immediately presents itself is why it does not occur from hydrocarbon films such as parafin. Other coatings that do not exhibit the desorption effect are the crown ethers. It appears that Si atoms in the polymer framework are necessary. One of the differences between the siloxanes and the crown ethers is the anticipated lower energy of the unoccupied electronic orbitals for the siloxanes. Since photodesorption appears to be associated with the



$$\left[-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-\right]$$

backbone, arranged either in rings or in linear polymer chains [1], the following charge-transfer reaction emerges as a reasonable hypothesis for the adsorption:

$$\mathrm{Na\,(gas)+PDMS\,(solid)\rightarrow Na^{+}PDMS^{-}(solid)}.$$

The alternating oxygen atoms in the PDMS backbone can serve to stabilize the Na^+ cation by complexation. Such Na^+ stabilization is common with crown ethers, which are sometimes used to put alkali cations into solutions of organic solvents. In addition to the energy stabilization upon complexation of Na^+ by several O atoms of the PDMS polymer, there is energy stabilization arising from the electronegativity of the PDMS. This is expected to be significant, especially if the electron from a neutral Na atom can be delocalized onto a number of Si atoms in the PDMS polymer. If such is the case, the low-lying empty Si orbitals would form a basis for a highly degenerate set of levels that can accept the alkali-metal electrons.

In the absence of the above charge transfer, the Na-PDMS interactions would be a much smaller physisorption with energies dominated by the polarizability of the Na atom and the PDMS film. These considerations are incorporated in the potential energy schematic shown in Fig. 3 where the correlations with separated neutral and ionic states of the system are shown. The two limits for the separated species are (1) a ground-state gaseous Na atom together with the neutral PDMS solid film, and (2) a ground-state gaseous Na^+ cation and the $PDMS^-$ solid film with its delocalized electron. As the neutral Na atom approaches the neutral PDMS surface, a van der Waals-type of binding would occur if no charge transfer takes place. As the Na^+ cation approaches the negative charge of the $PDMS^-$, the potential energy curve would follow the Coulomb law but would also likely have a contribution from ion-dipole forces at the equilibrium minimum-energy position. Since an interaction is expected between the two configurations, neutral and ionic, an anticrossing of the two corresponding potentials, van der Waals and Coulombic, occurs as indicated in Fig. 3. The ground state of the adsorbed species is expected to be the charge transfer complex Na^+ $PDMS^-$.

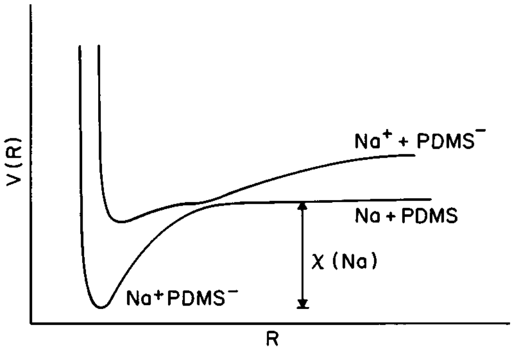
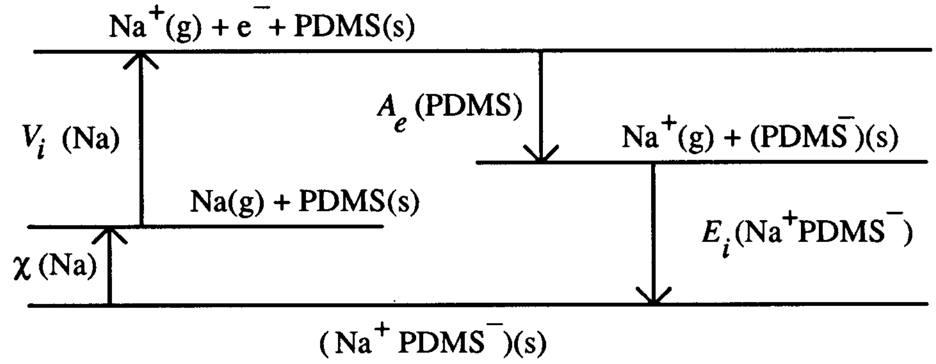


FIG. 3. Qualitative potential energy schematic for the charge-transfer model for the adsorption-photodesorption of Na atoms and a PDMS film. R represents the distance of the Na atom or Na^+ cation from the surface, and χ is the energy threshold.

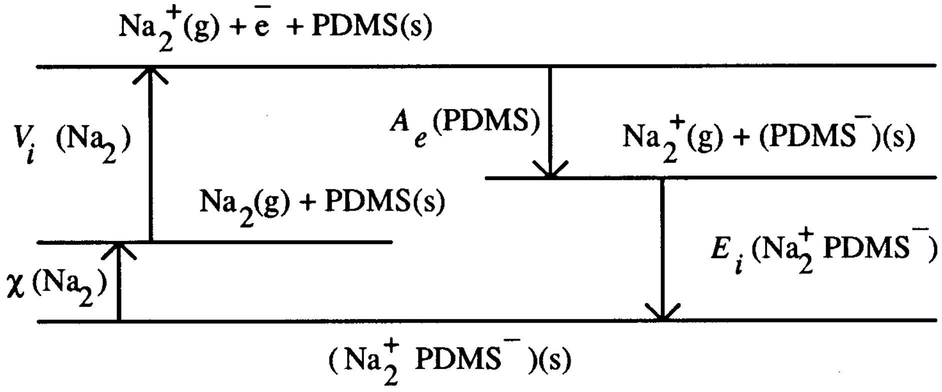
Absorption of radiation induces a reverse charge-transfer excitation to produce NaPDMS with negligible change in nuclear coordinates (distance of Na from the surface). NaPDMS is represented by the upper potential minimum in Fig. 3. If the excitation has sufficient energy above the upper-state minimum, the subsequent fast nuclear dynamics will follow a diabatic curve crossing over to the lower curve and a separation of neutral Na from the surface. The conditions that determine whether the dynamics will follow a diabatic curve are subject to the same Landau-Zener arguments that in the past have been applied to nonadiabatic molecular dynamics [6]. If the excitation does not have enough energy to overcome the interaction responsible for the anticrossing, the excited state will be trapped on the upper adiabatic curve as shown in Fig. 3 until it either undergoes dark relaxation or luminescence in a return to the ground state of the Na^+PDMS^- complex.

V. ENERGETICS OF SODIUM ATOM VS DIMER PHOTODESORPTION

A similar scheme to the one just presented in Fig. 3 holds for the Na_2 dimer. As the neutral molecule approaches the surface, an electron is transferred from it into the delocalized levels originating from the empty, low-lying Si orbitals, leaving a Na_2^+ cation to be complexed by the O atoms in the PDMS. With only a few reasonable assumptions, the energetics of the Na and Na_2 photodesorption thresholds can be summarized by the two following energy cycles:



and



where V_i is the ionization potential of the gas phase species, χ is the photodesorption threshold, A_e (PDMS) is the electron affinity of the PDMS, and E_i is the ionic binding energy of the gaseous cation with the negatively charged solid PDMS surface. Of these quantities, the V_i is known very accurately for Na and Na_2, and the photodesorption threshold is a measured result of the present experiments. For both Na and Na_2 the A_e (PDMS) is expected to have the same value, and E_i $Na^+(PDMS^-)$ should be nearly the same as $E_i(Na_2{}^+PDMS^-)$. It is true that the sizes of Na^+ and $Na_2{}^+$ are slightly different, but the Coulombic binding between the $PDMS^-$ and the two cations should be quite similar if the $PDMS^-$ structure is not significantly changed when $Na_2{}^+$ is substituted for Na^+. If it can be assumed that A_e and E_i do not change as Na^+ is replaced by $Na_2{}^+$, then

$$V_i(\mathrm{Na})+\chi(\mathrm{Na})=V_i(\mathrm{Na}_2)+\chi(\mathrm{Na}_2),$$

which can be expressed in terms of the difference in photodesorption thresholds

$$\chi(\mathrm{Na}_2)-\chi(\mathrm{Na})=V_i(\mathrm{Na})-V_i(\mathrm{Na}_2).$$

Indeed, one finds that the difference in ionization potentials [7,8]

$$V_i(\mathrm{Na})-V_i(\mathrm{Na}_2)=41\,449.65-39\,497.92\ \mathrm{cm}^{-1}$$
$$=1951.83\ \mathrm{cm}^{-1}$$

is nearly identical with the measured difference in experimental photodesorption thresholds:

$$\chi(\mathrm{Na}_2)-\chi(\mathrm{Na})=11\,500-9500=2000\ \mathrm{cm}^{-1}.$$

This measured threshold energy difference is consistent with the charge-transfer model presented above.

VI. LIGHT FREQUENCY DEPENDENCE OF THE DESORPTION YIELD

Besides the threshold behavior, another aspect of the present phenomenon where there appears to be a similarity with the photoelectric effect is the dependence of the photodesorption yield on the desorbing light frequency. As described above, a reasonable structure for the adsorbed Na atom on the PDMS surface is the charge-transfer formation of a Na^+ cation, stabilized by complexation with a ‘‘nest’’ of O atoms belonging to the polymer. A similar charge-transfer structure holds for adsorbed sodium dimers. For Na, the atomic valence electron can be delocalized into a set of energy levels (or possibly a band) originating from a basis of low-lying empty orbitals of the Si atoms of the polymer.

Absorption of light produces a reverse charge-transfer transition of the electron from its delocalized or ''band'' states to the Na^+ cation, thereby neutralizing it with enough energy left over to enable it to cross the energy barrier into free space as schematically displayed in Fig. 3 and discussed above. This concept incorporates the threshold feature of the experimental observations. It also presents the possibility of describing the electron transfer process in terms of the same theoretical treatment that has been so successfully applied to the photoelectric effect. Accordingly, the photoelectric effect treatments of Fowler [4] and DuBridge [5] can be used as a guide to examine the analogous dependence of the Na or Na_2 desorption yield on the incident-photon frequency.

Using Fermi-Dirac statistics for the thermal energy distributions for the delocalized electrons in a metal, Fowler was able to express the photoelectron yield as a function of temperature, photon energy $h\nu$, and work function χ. In most of the experiments done at the time of Fowler's analysis, the photon energies were comparable to the work function. Because of the mathematical complexity, the Fowler result had two forms: one for photon energies $h\nu\leqslant\chi$ and one for $h\geqslant\chi$. In the present photodesorption experiments the photon energy is always greater than the energy threshold. For this situation, the Fowler expression for the photoelectron yield is [4]

$$S=\frac{4\pi mk^2T^2}{h^3}\left[\frac{\pi^2}{6}+\frac{1}{2}\delta^2-\left\{e^{-\delta}-\frac{e^{-2\delta}}{2^2}+\frac{e^{-3\delta}}{3^2}-\cdots\right\}\right], \tag{1}$$

where $\delta=(hv-\chi)/kT$ and $\delta\geqslant 0$. When δ is significantly larger than zero, Eq. (1) predicts that the photoelectron yield will have an $(A+\delta^2)$ dependence on δ at constant temperature where A is a constant.

In the present case, if the delocalized electrons are appropriately described by the Fermi-Dirac distribution, then the charge-transfer excitation followed by desorption is analogous to the excitation of electrons in the photoelectric effect. The atomic desorption yield as a function of desorbing light frequency would follow the Fowler treatment, and for the case where $\delta > 0$ the atomic yield would have a $(A+\delta^2)$ dependence. As the Na desorption yield is measured by LIF, this suggests that a plot of the square root of the atomic LIF intensity against $h\nu$ (or $1/\lambda$) should exhibit a linear relationship, and an extrapolation to zero Na fluorescence intensity should give a value of $h\nu_0=\chi$, the threshold energy. A similar treatment for Na_2 would yield a threshold for that species. This has been done in Fig. 2 where the data exhibit a reasonably linear variation of $1/\lambda$ with the square root of fluorescence intensity and a threshold value at $I_f=0$ for each species.

VII. SUMMARY

The difference in photodesorption thresholds between Na and Na_2 adsorbed on PDMS films can be explained in terms of the energies associated with a model in which the adsorption process consists of the formation of a charge-transfer complex $\mathrm{Na}^+\mathrm{PDMS}^-$ in which the Na^+ is stabilized by interaction with several O atoms of the PDMS backbone. The Na valence electron is very likely delocalized into orbitals having the low-lying Si atomic orbitals as a basis. The photodesorption takes place by a reverse charge transfer that produces a neutral Na atom with enough energy to be ejected from the PDMS surface.

A number of very provocative and challenging questions remain to be answered such as whether the translational kinetic energy of the leaving atom is proportional to the ejection light frequency. The other extreme would be a thermal distribution for the ejected Na or Na_2. Further tests of the model as well as characterization of the surface are desirable. Additional support for the model can be gained from experiments on other alkali metals where the difference in threshold energies between atoms and dimers should be similar to the corresponding difference in ionization potentials. Studies on these and other adsorbed species will also permit an investigation of the extent of the analogy with the photoelectric effect that so far has been remarkable.

ACKNOWLEDGMENTS

This research was performed under the auspices of the Italian Institute of Physics of Condensed Matter (INFM). Financial support from the National Science Foundation and Consiglio Nazionale delle Richerche is gratefully acknowledged.

---

[1] A. Gozzini, F. Mango, J. H. Xu, G. Alzetta, F. Maccarone, and R. A. Bernheim, Nuovo Cimento D **15**, 709 (1993).
[2] A. N. Nesmeyanov, *Vapor Pressure of the Chemical Elements* (Elsevier, Amsterdam, 1963).
[3] M. Meucci, E. Mariotti, P. Bicchi, C. Marinelli, and L. Moi, Europhys. Lett **25**, 639 (1994).
[4] R. H. Fowler, Phys. Rev. **38**, 45 (1931); *Statistical Mechanics* (Cambridge University Press, Cambridge, 1955), p. 358.
[5] L. A. DuBridge, Phys. Rev. **43**, 727 (1933).
[6] R. B. Bernstein, *Chemical Dynamics via Molecular Beam and Laser Techniques* (Oxford University Press, Oxford, 1982), Chap. 8.
[7] C. E. Moore, *Atomic Energy Levels*, Natl. Bur. Stand (U.S.) Circ. No. 467 (U.S. GPO, Washington, D.C., 1949).
[8] C. Bordas, P. Labastie, J. Chevaleyre, and M. Broyer, Chem. Phys. **129**, 21 (1989).