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Surface-induced vibrational transition of metastable nitrogen molecules passing through a nano-slit grating

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Abstract. – Metastable nitrogen molecules N_2^* ($A^3 \Sigma_u^+$) passing through a Si₃N₄ nano-slit grating (slit width: 50 nm) experience elastic and various inelastic processes, due to diagonal and off-diagonal interactions with the solid surface at short and intermediate distances (10–100 a_0), *i.e.* mainly interactions of the van der Waals (vW) type. These processes are observed by use of a velocity selected beam and a time-of-flight analysis combined with angular measurements of scattered metastable molecules. The main feature is the occurrence of an inelastic exothermal process identified, by both its kinetic energy gain and angular dependence, as being a vibrational transition with $\Delta v = -1$. A semi-classical model using a calculated (vW) dispersion energy depending on the orientation of the molecule and the vibrational coordinate is proposed.

Making atoms or molecules pass in the vicinity of a nano-structured solid is a powerful experimental tool to enhance and better observe interactions with the surface as well as to investigate various spectroscopic effects dealing with confinement [1]. A nano-slit grating (in the present case 50 nm wide slits with a 100 nm period) appears as being particularly well adapted to the case of a *beam* of atoms or molecules since atoms or molecules are constrained to fly at a small distance z from the walls ($z \leq 25$ nm in our case), which makes a large fraction of them participate in the interactions with the surface in the so-called intermediate distance range (from a few nm up to a few hundreds of nm) where the non-retarded van der Waals (vW) interaction dominates. Moreover, provided that the collimation of the beam is sufficient to make the transverse size of the wave packet wider than the grating period, a coherent matter wave diffraction is observed [2–4]. It has been shown [3] that because of the vW interaction the

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Fig. 1 – Scheme of the experiment. S: metastable N₂* molecule pulsed source; SD: slotted disk for velocity selection ($\delta v/v = 8\%$); G: nano-slit grating; D: detector. The distance SG is $L_1 = 121$ mm; the distance GD is $L_2 = 164$ mm. The grating slits are vertical to the drawing plane.

effective width of the slits is smaller than the geometric one, which leads to significant changes in the intensities of the diffraction orders. In the present work the rather wide angular spread of the incident beam ($\Delta \theta \approx 1.4^{\circ}$) will *not* allow us to observe similar effects: here the grating simply serves to enlarge the active surface area and to enhance the number of molecules passing at a small distance from the surface. In this type of experiments long-lived excited states (metastable atoms or molecules) are particularly attractive, not solely because they are easy to produce and detect (at least when their internal energy is larger than 5–6 eV) but also because they are expected to have a much stronger interaction with surfaces than ground-state species. In the present paper, the interaction of a thermal beam of metastable nitrogen molecules (N₂*, $A^{3}\Sigma_{u}^{+}$) with a silicon-nitride nano-slit grating is studied. Several processes are observed: elastic collisions resulting in a narrowing of the angular profile, an endothermal process at small angle, an exothermal process identified as a vibrational transition ($\Delta v = -1$) which appears at large scattering angles. This latter process will be analyzed in some detail in this letter. It is a vibrational counterpart to the electronic ${}^{3}P_{0}{}^{-3}P_{2}$ transition induced by the quadrupolar part of the vW interaction, recently observed in Ar* and Kr* metastable atoms [5].

Metastable N_2^* (A ${}^{3}\Sigma_{\mu}^+$) molecules are produced by electron bombardment of an effusive beam of ground-state molecules. The electron energy is limited to 35 eV to avoid the production of other long-lived excited molecular states $(W^{3}\Delta_{\rm u}, A'^{5}\Sigma_{\rm g}^{+})$ and too large a dissociation rate leading to N* metastable atoms [6]. Having in view to identify collision processes from kinetic energy losses or gains, the primary beam is velocity selected ($\delta v/v \approx 8\%$) by use of a double chopping technique (pulsed electron gun followed by a synchronized slotted disk). Metastable molecules are then detected in the time-of-flight (TOF) operating mode. The detector consists of a secondary emission aluminium plate followed by a channel electron multiplier. The internal energy of the $A^{3}\Sigma_{u}^{+}$ state (6.17 eV [7]) is large enough to give an efficient secondary electron emission from the metal. The overall detection efficiency for N_2^* molecules is about 10%. It is higher ($\approx 40\%$) for far UV photons ($\lambda < 140$ nm). The detector is set on a rotary platform, at a distance $L_2 = 164 \text{ mm}$; the source-grating distance is $L_1 = 121 \text{ mm}$ (see fig. 1). The silicon-nitride grating actually consists of 3 sets of nano-slits placed within 3 vertical 1 mm wide, 4 mm high slits. In order to avoid any spurious effect on the velocity selection, only the central large slit is used. The grating itself is ideally made of a series of vertical parallel square bars $(50 \times 50 \,\mathrm{nm^2})$. Actually the sections of these bars are slightly trapezoidal [3] and the corrugation of the surfaces, as given by the manufacturer, is of the order of a few nm.



Fig. 2 – Differential cross-section (in arbitrary unit) for the superelastic process as a function of the scattering angle θ . The initial velocities are 883.5 m/s (full line) (the kinetic energy is $E_0 = 118.0 \text{ meV}$) and 641 m/s ($E_0 = 63.3 \text{ meV}$) (dotted line). The vertical arrows show the predicted angular locations of the inelastic process $v \rightarrow v - 1$, with $\Delta E = 172 \text{ meV}$ (v = 5). Inset: full line: TOF spectrum at $v_0 = 883.5 \text{ m/s}$ and $\theta = 50^{\circ}$. One channel corresponds to $3.3 \,\mu$ s. The vertical arrows show the predicted positions of the inelastic peak for $\Delta E = 140 \text{ meV}$ (v = 9) and 172 meV (v = 5); dotted line: incident TOF spectrum (its height has been divided by 100).

The expected geometrical angular spread of the emerging beam, derived from the transverse size of the source (2 mm in diameter), the width of the grating (1 mm) and the width of the detector entrance slit (0.3 mm) is $\Delta\theta_{\rm G} = 1.43^{\circ}$. This angular spread has been measured previously, the grating being replaced by a 1 mm wide slit. The measured value, $1.42 \pm 0.2^{\circ}$, determined by a Gaussian fit of the angular profile, is in good agreement with this calculation. Actually the observed profile ($\Delta \theta = 1.0 \pm 0.2^{\circ}$) is narrower than this natural width. This is a manifestation of the (elastic) vW interaction, similar to that already observed in the diffraction regime for ground-state species [3]. A quantitative interpretation of this phenomenon, which has also been observed with metastable rare-gas atoms, will be given in a forthcoming paper. In the small-angle range ($|\theta| \leq 6^{\circ}$) the TOF spectra exhibit, in addition to the purely elastic contribution, two inelastic processes. The first one, corresponding to a well-defined TOF close to the value L_1/v_0 , can be attributed to detected far uv photons, emitted from the grating by radiative excited states of N₂ produced by surface-induced electronic transitions, reaching the detector after a negligible time of flight (L_2/c) . The second process, related to a wide structure in the TOF spectra, located at TOFs larger than the selected one, corresponds to unresolved rotational transitions. The differential cross-section for this process (it is actually a sum of differential cross-sections related to individual rotational excitations) shows regular damped oscillations as a function of the scattering angle θ , suggesting a multi-path interference phenomenon similar to Stueckelberg oscillations.

At the two incident velocities considered here, $v_0 = 883.5 \text{ m/s}$ and 641 m/s (the corresponding initial kinetic energies are $E_0 = 118.0$ and 63.3 meV), the most prominent inelastic feature appears at large angle ($\theta > 40^\circ$). It is an exothermal process, the TOF of which (inset in fig. 2) corresponds to an energy gain $\Delta E = 160 \pm 40 \text{ meV}$, a value consistent with the vibrational constant of the $A^{3}\Sigma_{\rm u}^{+}$ state: $\omega_{\rm e} = 181 \text{ meV}$ [7]. Actually, from the Franck-Condon

principle, the vibrational distribution in the incident beam is expected to range from level v' = 5 up to v' = 9, the energy interval between subsequent vibrational levels decreasing from 172 down to 140 meV (the TOFs for these two values of ΔE are shown in fig. 2). On the other hand, rotational populations in the metastable-molecule beam are difficult to determine. Nevertheless, as will be seen further, rotational excitations and de-excitations induced by the vW interaction are also expected to occur. Finally, the only molecular transitions that can be reasonably made responsible for the observed process are of the type: $(v', J') \rightarrow (v'-1, J)$, with $v' \geq 5$. The angular distribution confirms the existence of this exothermal process. Since the interaction with the surface only depends on the z coordinate of the center of mass (z being the normal to the surface), the component of the total momentum parallel to the surface is conserved which gives rise, for a perfectly planar surface and a well-defined value of ΔE , to a deflection angle $\theta_f = \tan^{-1}(\Delta E/E_0)^{1/2}$, where E_0 is the incident kinetic energy. As is seen in fig. 1, the differential cross-sections (area of the TOF peak as a function of θ) exhibit at both incident velocities a maximum close to the θ_f value calculated with $\Delta E = 172 \text{ meV}$. The shape of the TOF spectra does not depend much on θ , except at $\theta = 45^{\circ}$, *i.e.* at an angle for which the molecules graze one edge of the slit and then the opposite edge. At this angle the spectrum becomes as narrow as the incident one. So far no clear explanation of this singularity has been found. The total inelastic flux represents about 5% of the flux emerging around $\theta = 0^{\circ}$ (which is itself about 10% of the total incoming flux). The rather large width of the observed angular distributions (17° and 19° at $E_0 = 118$ and 63.3 meV) comes from uncertainties on v', J', J and from the surface roughness. The uncertainty on v' leads to angular spreads of 2.9° and 2.6° at the two present energies, and the uncertainties about J'and J are expected to contribute by much smaller amounts. Hence the main contribution is that of the roughness of the solid surfaces, roughness in a general sense, namely any random or systematic [3] defect with respect to the ideal shape. The standard deviation of the surface with respect to a perfect plane (along the direction of the beam axis) is estimated by the manufacturer to be a few nm. However the (unknown) spatial-frequency spectrum of the corrugation plays also a role, as it does in the reflection of cold atoms on a surface [8], since in the present case the angular spread is directly related to the dispersion of the slope of the tangent planes. It is worth noticing that the present method is able to probe the surface corrugation "in depth", *i.e.* in a direction perpendicular to the grating plane. To these purely random effects it is likely that systematic effects should be added, e.g. that of the inclination of the walls with respect to the z-axis.

This part of the paper will be devoted to the theoretical interpretation of the vibrational de-excitation process. As will be seen further, because of the complexity of this collisional process, we shall use severe simplifications and finally obtain a reasonable but relatively poor agreement with experiment. Nevertheless, as it is, this calculation has the merit to explain the basic mechanism and to show that a rather strong rotational alignment (not experimentally observed here) of the emerging molecules can be achieved. The ability of the vW dispersion interaction U_d to induce rovibrational transitions comes from the fact that it depends on both the orientation of the molecular axis and the vibration coordinate. The (dominant) dipolar contribution to the energy is [9]

$$U_{\rm d} = -\frac{\hbar}{16\pi Z^3} \int_0^\infty \mathrm{d}\xi \Delta(i\xi) \left[\left(3\alpha_\perp(i\xi) + \alpha_\parallel(i\xi) \right) + \left(\alpha_\parallel(i\xi) - \alpha_\perp(i\xi) \right) \cos^2\Theta \right],\tag{1}$$

where Z is the distance from the molecule center to the surface, $\Delta = (\varepsilon - 1)/(\varepsilon + 1)$ is the reflection factor of the solid, where ε is the dielectric constant, $\alpha_{\perp,\parallel}$ are the perpendicular and parallel polarisabilities (referred to the molecule axis z') and Θ is the angle between z and z'.

According to the Drude model, $\alpha_{\perp,\parallel}(i\xi) = \alpha_{\perp,\parallel}(0)(\omega_{\perp,\parallel}^0)^2[\xi^2 + (\omega_{\perp,\parallel}^0)^2]^{-1}$, where $\omega_{\perp,\parallel}^0$ are characteristic frequencies. A similar expression for $\Delta(i\xi)$ is obtained using the Clausius-Mossotti formula, with a characteristic frequency $\omega_{\rm s}$. Let us assume, for the sake of simplicity, that $\omega_{\perp}^0 \approx \omega_{\parallel}^0 = \omega_0$ (according to numerical values found in the literature, this is a reasonable assumption). On the other hand, *ab initio* calculations performed on some simple molecules [10] as well as semi-empirical calculations based upon the shape of the molecular bound density [11] show that the static polarisabilities and then the dispersion energy depend on the internuclear distance r. For v' = 5, the vibrational coordinate $\zeta = r - r_{\rm e}$ can be considered as relatively small $(-0.16 \leq \zeta \leq 0.19 \,\text{\AA})$ compared to $r_{\rm e} = 1.29 \,\text{\AA}$. Finally the dispersion energy takes the form

$$U_{\rm d}(Z,\Theta,r) \approx U_{\rm d}(Z,\Theta,r_{\rm e}) + \zeta \left[\frac{\partial U_{\rm d}}{\partial r}\right]_{r_{\rm e}} = -f(Z)V(\Theta,\zeta),\tag{2}$$

where

$$f(Z) = \frac{\pi\hbar}{16}\alpha_{\rm s}(0) \left(\frac{\omega_{\rm s}}{\omega_{\rm s}'}\right)^2 \frac{\omega_0}{\omega_{\rm s}' + \omega_0} Z^{-3}$$
(3a)

and

$$V(\Theta,\zeta) = (A + B\zeta) + (D + E\zeta)\cos^2\Theta; \qquad (3b)$$

 $\alpha_{\rm s}(0)$ is the static polarisability of the atoms in the solid and $\omega'_{\rm s} = \omega_{\rm s} [1 + \frac{2\pi}{3} \alpha_{\rm s}(0)]^{1/2}$ is the surface resonance frequency. Numerically the constants are as follows (in atomic units): F = 0.0173 [12]; A = 51.33; B = 5.32; D = 12.20; E = 28.00. The latter coefficients are calculated assuming a factorized form of the rovibrational wave functions (see below).

As the de Broglie wavelength associated to the center-of-mass motion is small even at a nanometric scale ($\lambda = 1.6 \cdot 10^{-2}$ nm at $v_0 = 883.5$ m/s), a classical treatment of this motion is valid. Moreover the rotational frequencies $(\nu_J = 4.3J(J+1) \text{ GHz}, \text{ with } J \text{ ranging from about}$ 3 to 10) and a fortiori the vibrational ones $(4.36 \cdot 10^{13} \text{ Hz})$ are large compared to the inverse of the transit time through the grating (17.6 GHz at $v_0 = 883.5 \,\mathrm{m/s}$). As a consequence, the distance Z(t) to the surface can be determined using a potential \overline{U}_{d} averaged over r and Θ . In the present case (all quantities are in atomic units), one has $\bar{U}_{\rm d} \approx -1.0/Z^3$ and $Z(t) \approx \rho [1 - t^2/(14335\rho^5)]^{1/2}$, where ρ is the impact parameter. Then Z(t) can be considered as a parameter in the time-dependent Schrödinger equation governing the internal molecular motion. In fact in this approach a single classical trajectory, common to all channels (v, J), is implicitly assumed. This is verified for states having the same v and different J's, but it is far from being true for different vibrational states, for example states v and v-1, since the transition is accompanied by a kinetic energy gain larger than E_0 and a large deflection angle. A trick similar to that already used for metastable atoms [5] will allow us to avoid this difficulty: introducing a width γ on the lower vibrational state (γ^{-1}) being of the order of magnitude of the time needed by the molecule to fly away from the coupling region, *i.e.* of the order of a few 10^4 au) provides a way to eliminate the second part of the trajectory. The wave function $|\psi\rangle$ being expanded over the basis set of the eigenfunctions $|v, J, M\rangle$ of the rovibrational Hamiltonian H_0 , the Schrödinger equation is transformed into a set of coupled equations for the amplitudes $a_{vJM}(t)$. Assuming the factorization $|v, J, M\rangle = |v\rangle \otimes |J, M\rangle$, the rotational coupling terms are proportional to $\langle J, M | \cos^2 \Theta | J', M' \rangle$. As $\cos^2 \Theta$ is a linear combination of spherical harmonics Y_0^0 and Y_2^0 , one gets the selection rules M' = M and $J' = J, J \pm 2$ (the symmetry of the molecule forbids transition to $J \pm 1$). Since the vibrational



Fig. 3 – Calculated transition probabilities as functions of the impact parameter ρ , for $\gamma = 10^{-3}$ au, $z_0 = 5$ au, $v_0 = 883.5$ m/s. Full line, solid circles: averaged probability P; dotted line, open circles: normalized alignment coefficient ΔP (see text).

splitting ΔE is larger than the incident kinetic energy E_0 , all vibrational excitation channels are closed. We shall consider that the only de-excitation channel is $v \to v - 1$. Assuming for J the lowest possible value, the problem involves only 3 states: $|v, J, M\rangle$, $|v - 1, J, M\rangle$, $|v - 1, J + 2, M\rangle$, respectively labeled 1, 2, 3. The introduction of the width γ simply consists in replacing H_0 by $H_0 = H_0 - i\gamma(|2\rangle\langle 2| + |3\rangle\langle 3|)$. All matrix elements of the interaction are of the form $U_{ij} = -A_{ij}Z^{-3}$. The numerical values of the coefficients (in au) are as follows (the first value corresponds to M = 0 and the value in parenthesis to $M = \pm 1$): $A_{11} =$ $A_{22} = 1.014 (0.930)$; $A_{33} = 0.907 (0.890)$; $A_{12} = 0.0335 (0.0165)$; $A_{13} = 0.0192 (0.0171)$; $A_{23} = 0.943 (0.933)$. The coupled equations have been solved for times ranging from t = 0, *i.e.* when the center of mass of the molecule enters the potential, to $t = t_0$, *i.e.* when the center of mass arrives at a distance z_0 to the surface under which the quenching of the metastable state is supposed to surely occur ($z_0 \sim 5$ au). Then the quantity $P_{|M|}(\rho) = 1 - ||\psi(t_0)||^2$ is the probability that a molecule in state 1 (M = 0 or ± 1), coming in at an impact parameter ρ , escapes in the vibrational state v - 1.

For a "natural" (*i.e.* neither aligned nor oriented) incident beam, the transition probability takes the mean value $P(\rho) = \frac{1}{3}(P_0 + 2P_1)$. On the other hand, the normalized coefficient $\Delta P = (2P_1 - P_0)/(2P_1 + P_0)$ measures the rotational alignment in the outgoing molecular beam. Figure 3 shows P and ΔP as functions of ρ calculated at an incident velocity of 883.5 m/s, with $\gamma = 10^{-3}$ and $z_0 = 5$ au. The ratio ρ_e/w , where, $\rho_e = \int_{z_0}^{\infty} P(\rho) d\rho$ and w is the slit width, represents the fraction η of the incoming molecular flux passing to the inelastic channel. One obtains here $\eta = (1 \pm 0.3) \cdot 10^{-3}$, a value somewhat lower than the experimental one: $\eta \approx (5 \pm 1.5) \cdot 10^{-3}$. It is likely that this discrepancy comes from the crude simplifications introduced in our model, in particular the restricted number of participating rotational states and the absence of any contribution of quadrupolar moment of the molecule to the interaction, two assumptions which are expected to reduce the value of η .

In conclusion, using a velocity-selected beam and combining time-of-flight and angular measurements, we have shown for the first time that a significant fraction ($\sim 0.5\%$) of

metastable N_2^* $(A {}^3\Sigma_u^+)$ molecules traversing a nano-slit grating experience a surface-induced vibrational de-excitation making them scatter at large angles. This process, which is the rovibrational counterpart of the surface-induced ${}^3P_0 {}^{-3}P_2$ transition of metastable rare-gas atoms, is caused by the dependence of the vW interaction on both the internuclear distance and the orientation of the molecule. The angular analysis of such surface-induced exothermal processes in metastable atoms or molecules provides us with a probe of the surface roughness along a direction perpendicular to the plane of the grating, *i.e.* along the thickness of the slits. This type of surface-induced superelastic process is not restricted to electronic transitions in atoms or vibrational de-excitation of molecules. It applies to any exothermic transition provided that the incident kinetic energy matches the energy gain. Such an inelastic molecular diffraction from transmission gratings has recently been proposed as a way of studying excited He₃ molecules [13].

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