

SF₆ scattering from graphite surfaces: comparison of effects induced by thermal and laser controlled vibrational excitation

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Abstract: We report scattering experiments of multiphoton vibrationally excited SF₆ molecules from graphite surfaces demonstrating ro-vibrational excitation in the collision. The beam scattering experiments were carried out at different initial kinematic conditions and as a function of the surface temperature. The energy transfer depends both on the initial state of the molecule and on the momentum transferred as well as on the temperature of the surface. The role of surface atomic corrugation is evidenced.

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1. Introduction

The understanding of the dynamics of the interaction of excited molecules with solid surfaces is very important to clarify physical and chemical processes of fundamental and applied

interest such as physisorption, chemisorption and heterogeneous catalysis. The comprehension itself of gas-surface chemical dynamics relies on the understanding of the different elementary processes such as energy transfer, diffusion and reaction that are often strongly coupled. Studies focusing separately on the different steps in selected systems have therefore acquired an increasing importance. In this framework energy transfer between non-reactive partners has enjoyed relevant attention and great progresses have been made in the last decade or so even though these studies are still restricted to simple molecules and a limited number of surfaces. This has driven an increasing interest towards collision experiments of ro-vibrational excited molecules with well-characterised surfaces. Advances in the understanding of the role of molecular vibrations are reviewed by Houston and Merrill [1], and by Rettner et al [2]. There are very few examples of studies involving molecules larger than diatomic or triatomic due to the difficulties inherent in the experimental analyses of the final ro-vibrational state of the molecule after scattering because of the too high vibrational densities of states and the rotational congestion in polyatomic molecules.

An interesting original approach has been adopted by Andersson et al. in studying the inelastic scattering and vibrational excitation of SF₆ from graphite surfaces [3]. They determined the final vibrational temperature of the scattered molecules by monitoring the ratio of the yields of the fragment ions produced by electron impact. The relative abundance of the fragments is in fact a sensitive indication of the vibrational excitation of the parent molecule. Besides the fundamental aspects, the study of the interaction of SF₆ with solid surfaces is of particular interest since its excited species could be efficiently and selectively used in processes of technological interest [4,5]. A relevant experimental point is that beams of highly vibrationally excited molecules are efficiently prepared by CO₂ multiphoton excitation and have been studied in detail [6,7].

In previous SF₆ scattering experiments on a GaSe (001) surface [8,9], we have investigated the role played by the internal degrees of freedom in the molecule-surface energy transfer processes. We concluded that only the coupling between the internal state of the molecule and the momentum transferred during the collision could explain the observed trends in the angular and intensity distributions. Because of the large corrugation of the GaSe surface, the assumption that the parallel momentum is conserved during the collision breaks down so that the information on the angular position of the lobe and on the energy exchanged during the collision could not be deconvoluted directly from kinematics.

In the present work on graphite (HOPG), we take full advantage of an optothermal detection scheme to study directly the energy transferred during the collision of multiphoton excited SF₆ molecules. Our angular resolved measurements, giving information on both momentum and energy transfer, allow to investigate the coupling of the different degrees of freedom during the collision. In this framework the use of different type and degree of excitation of the incident molecule reveals the presence of significant state selectivity.

2. Experimental

The experimental set-up is the same used in previous experiments [8] and consists of a main scattering chamber and a cluster of different beams and analytical tools. The UHV scattering chamber is characterised by two levels: one where the beam scattering experiments take place and the other where some basic surface characterisations are carried out. The beam level includes two cryogenic bolometers, rotatable with an accuracy of about 0.03°, with an acceptance angle of 0.6° and 1.2° respectively. The bolometer measures the energy released on its surface by the flux of particles hitting it. Detected signals are therefore proportional to the total energy of the particle reaching the detector. In fact the SF₆ molecules will all stick on the cold surface of the bolometer (1.5K) so that one can assume that the accommodation coefficient is 1 for all the different types of energies involved [10]. The cold shields around the bolometer have two holes which allow the molecules to pass through to be detected: one of them exposes the front of the detector to the centre of the sample and the other one looks

backward along the same direction. In this way we can measure with the same detector both, the signal due to the scattered particles, and, when rotated at the right angle, the main incoming beam before it collides with the surface. This is important in order to normalise correctly the observed intensities. In general, the angular distributions of the scattered molecules measured by a flux or density detector do not give direct information on both the transferred momentum and the energy exchanged during the collision unless an assumption is made on the conservation of the parallel momentum. Our approach is to measure the energy content of the molecules before and after the scattering process resolving the angular distribution of the molecules after the collision. This is our way to gather direct information on the energy exchanged in the scattering process when correctly analysed and normalised. In the present experiments the normalisation is done by taking the ratio between bolometric scattered intensity and the corresponding signal of the incident beam measured in the same experimental conditions.

A sample manipulator allows full control of the position of the surface along the three axes of rotation and the three translations. We perform high resolution He diffraction to obtain the required information about the orientation of the surface and its atomic corrugation. The He diffraction pattern is also used as a very sensitive measure of any adsorption, from the background gases or from the beams, that would pollute the surface.

The SF₆ beam is produced by a variable temperature standard supersonic source with temperature stability better than 1%. Time of flight measurements are used to accurately determine the initial kinetic energy of the beam. By accurately tuning the source temperature and the percentage of seeding in He we can easily explore kinetic energies ranging from 100 meV to about 600 meV. It is important to recall that, in a free jet expansion, source temperatures and seedings change also the beam's vibrational and, much more dramatically, rotational temperatures inducing the ro-vibrational cooling [10]. Boschetti et al. [6] showed that in the expansion of SF₆ the final rotational and translational temperatures are very close and low, whereas the vibrational temperature can be assumed close to the source temperature.

We use a high power CO₂ laser to induce a multiphoton vibrational excitation of the SF₆ molecules. The laser beam crosses the molecular beam orthogonally in the second stage of the differentially pumped beam set-up. The laser light is focused on the molecular beam by a 5 cm focal length salt lens in order to increase the laser fluence achieving a higher vibrational excitation. The fluence experienced by the molecules ranges from 160 to 290 mJ/cm² depending on the beam velocity keeping the laser power fixed at 90 W. SF₆ beams at different source temperatures are characterised by a radiation absorption intensity that depends on the laser frequency [6]. In the present experiments the CO₂ laser is tuned to the 10P26 line that gives a high absorption signal for all the source temperatures used. Under the highest fluences and depending on the source conditions, the molecules irradiated by the laser typically absorb 5 CO₂ photons each. This has been calculated using the method of Liedenbaum et al. [7] on the basis of the observed opto-thermal signals. We compared the amount of energy in the different degrees of freedom of the molecules in the beam regimes explored. The kinetic energy is varied from about 150 to 600 meV while the thermal excitation into vibrations of a pure beam is changed from about 280 to 700 meV (2300 to 5700 cm⁻¹), evaluated as in [6]. Since the typical laser induced excitation used is 600 meV, we really explore with the present experiments collision events where the role of the different degrees of freedom can be assessed.

3. Results and discussion

A first series of scattering experiments from graphite was devoted to monitor the energy transfer processes for thermal excited SF₆ beams. We carried out a large number of measurements as a function of the surface temperature and initial beam conditions. Figure 1a shows the polar plot of the normalised angular distribution of the bolometric signal of the scattered particles. The data shown correspond to three different surface temperatures. The

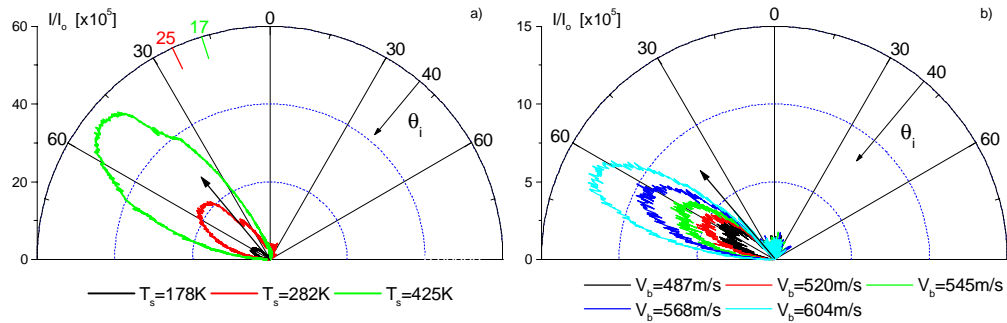


Fig. 1. a) Normalised angular distributions of scattered SF₆ molecules ($V_{\text{beam}}=520\text{m/s}$) for three different surface temperatures. b) Distributions of SF₆ beams scattered from the HOPG surface ($T_s=178\text{K}$) at different initial beam velocities. The arrows indicate the position of the incidence and specular angles ($\pm 40^\circ$ respectively). The coloured signs on the degree scale of fig. 1a show the angles calculated kinematically (see text).

angular distributions are characterised by two contributions: a lobular part peaked at angles close to the specular angle and a very small diffuse cosine-like part. This diffuse scattering is usually attributed to indirect inelastic and adsorption-desorption processes while the lobular structure is due to direct inelastic processes. The large increment of the normalised intensity of the direct inelastic lobe with increasing surface temperature is due to the larger uptake of energy by the molecule scattered from the hotter surface. Moreover the lobe angular position shifts towards the surface normal as the surface temperature is increased. This is consistent with a picture where the molecule acquires perpendicular momentum. We can assess the contribution to the energy transferred in the collision by assuming that during the scattering only the kinetic energy of the molecule would be effected. In this case, and assuming that the parallel momentum is conserved, one can predict kinematically the shifts of the lobes due to the energy transferred perpendicularly with respect to the lowest surface temperature. We calculated in this way the position of the maximum of the lobes for the two higher surface temperatures. They are indicated in figure 1a by the signs on the angle scale drawn in the same colour as the corresponding sets of data. The experimental shifts are much less than the kinematic predictions obtained from the relative energy transferred. There should therefore be a relevant flow of energy into the ro-vibrational modes that competes with the purely kinetic channel. This is consistent with the observations in the experiments on the GaSe surface [8].

The normalised angular distributions obtained for different beam source conditions are shown in figure 1b. These data are obtained at a surface temperature of 178K and show that for higher source temperatures the forward lobe grows considerably. This specific trend is similar to the one observed in the GaSe experiment. The molecular beams with more kinetic energy before the collision give rise to a higher energy uptake during the collision and an angular shift of the maximum of the lobe towards the surface. This trend is again inconsistent with a model involving only the kinetic energy transfer. In fact, still assuming parallel momentum conservation, there should be an increasing loss of perpendicular velocity of the molecule causing the observed lobe shifts as a function of the initial velocity. On the contrary the normalised intensities show more energy uptake of the molecule during the collision. This is another indication of the relevance of the internal degrees of freedom.

Our observed evidence that in the collision from a graphite surface there is an uptake of energy into ro-vibrations depending on surface temperature is somewhat unexpected if compared with the conclusions of Andersson et al. [3]. Their experiments show that SF₆ molecules experience a low but significant vibrational excitation during the collision, which depends only on the incident energy. They do not observe any effects due to the surface temperature. The apparent discrepancy maybe due to the different regimes explored in terms of initial beam characteristics and surface temperatures. Andersson et al. have used surface

temperatures from 950-1400K to be compared with the range 178-425K in our experiments. Furthermore the initial beam vibrational temperature is different. In Andersson's case it is about 300K while ours is varied with the source temperature from 500 to 850K. SF₆ is often considered a "sponge" from the point of view of the energy that can be stored into it. In particular it has been shown with multiphoton spectroscopy that the excitation efficiency increases when the temperature of the source is increased [6,7]. This ability of the SF₆ molecule of picking up energy when already "hot", that is when low lying hot bands are populated, may play an important role in the observed trends and can explain the difference in observations with Andersson et al. On the other hand scattering experiments of CF₃Br from graphite [11] have shown a significant vibrational excitation depending both on kinetic energy and surface temperature as in our case.

We recall that, since the beam velocity is varied by changing the source temperature, higher beam velocities correspond also to hotter molecules. We varied the internal energy of the beam before the collision without changing its velocity by CO₂ laser multiphoton excitation. The experiments were carried out by mechanically chopping the laser beam and by using Lock-In amplification in order to monitor the scattering of the multiphoton excited SF₆ molecules. Typical normalised angular distributions obtained with different beam conditions are shown in Figure 2a. Figure 2b illustrates the maximum of the normalised lobes as a function of the laser induced opto-thermal intensity of the incoming beam for two different beam conditions. We recall that the opto-thermal intensities measured are proportional to the average number of photons stored in the molecule before the collision. These data show that in the scattering from graphite the energy transferred at the surface is almost independent from the rate of laser excitation. The comparison between the two different beams however shows again that the molecules with a higher incoming kinetic energy (the 50% seeded beam) emerges with a larger uptake of energy after the collision. For comparison figure 2b shows also the data obtained on GaSe (open symbols) where the dependence from the amount of laser excitation is evident. The negative slope in this case indicates lower propensity to uptake energy by more strongly excited molecules. The different trends shown by the two surfaces are an indication that the energy transfer mechanism in the scattering of the laser excited molecules is surface specific.

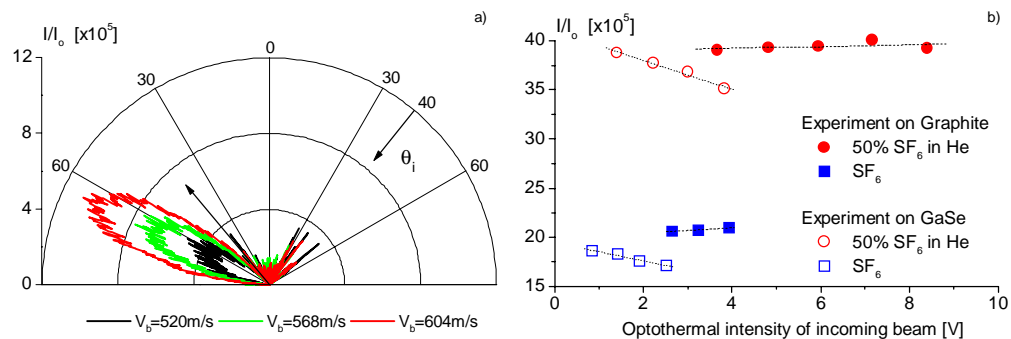


Fig. 2. a) Normalised angular distributions of laser multiphoton excited SF₆ molecules scattered from the graphite surface (T_s=178K) at different initial beam velocities. b) Normalised intensity of the lobes for the laser induced scattering signals of two different beams as a function of the opto-thermal intensity of the incoming beam (see text). The open symbols represent the data obtained on the GaSe surface while the closed symbols show the results from the graphite surface. The lines are shown just to guide the eye.

We mentioned before that the angular position of the maximum of the lobe changes with the beam average velocity. To qualify further this dependence, the position of each direct inelastic lobe is determined by fitting the form of the angular distribution by an appropriate

shape function. We have investigated the angular position of the maximum of the lobe as a function of the beam velocity and different molecular excitation. The results are shown in figure 3. These data show that a higher internal energy before the collision pushes the maximum of the lobe towards the surface. We believe that this is our major experimental result that demonstrates the coupling between internal excitation and momentum transfer in the collision. This behaviour is similar to that observed for GaSe. A major difference however is that for graphite the lobe position, at similar beam conditions, is shifted much more towards the surface. This could be due to the role played by the corrugation of the surface and the relative importance of parallel versus perpendicular momentum. As mentioned earlier, in the case of GaSe the conservation of parallel momentum is far from holding so that the energy exchanged is correlated to both components of the momentum. The larger scattering angles observed on graphite are consistent with substantial conservation of parallel momentum.

The different phonon structures between GaSe and graphite could also play a role in the energy transfer [12] and therefore deserves further investigation. We only mention here that the perpendicular surface Debye temperatures are not too different ($\theta_{D\perp} \approx 342\text{K}$ for GaSe [12] and $\theta_{D\perp} \approx 500\text{K}$ [13]) when compared to the temperature range explored in our experiments while the phonon spectra differ significantly [12].

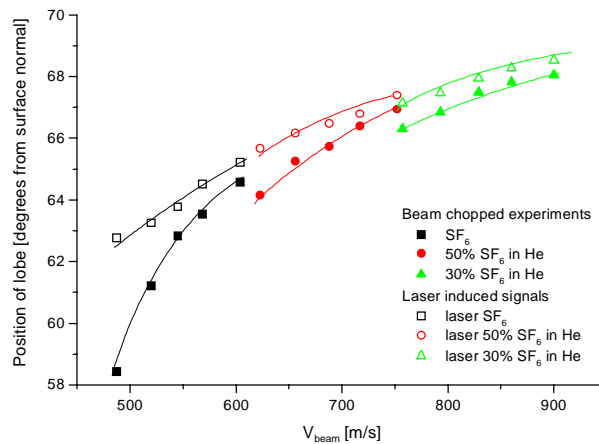


Fig. 3. Position of the maximum of the lobes (degrees from surface normal) as a function of the average beam velocity. The open symbols are for the laser induced angular distributions, while the closed symbols are from the results with the thermal beams. The angle of incidence is 40° ($T_s=178\text{K}$).

4. Conclusions

We observed effects of laser induced ro-vibrational excitation in the scattering of SF_6 beams from graphite. Laser excitation in the ν_3 mode produces direct inelastic scattering lobes different in position and energy transferred compared to thermal heated molecules. This is qualitatively interpreted as the effect of the coupling of the internal excitation to the momentum transferred during the collision. Similarities and differences with previous experiments on GaSe show surface sensitivity ascribed to the different corrugation even though further investigations are needed.

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