Quantum Electronics **36** (9) 889 – 894 (2006)

PACS numbers: 33.80.–b; 42.62.Fi; 82.40.Fp; 82.50.Fv
DOI: 10.1070/QE2006v036n09ABEH013252

Efficiency of passage of highly vibrationally excited CF_3I molecules in a beam through a cooled converging hollow truncated cone

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Abstract. **The passage of CF_3I molecules excited by high-intensity IR laser radiation to high vibrational states (with energy $E_v \geqslant 0.3 - 1.5$ eV) and unexcited molecules in a pulsed beam through a converging truncated hollow metal cone cooled to $T_s \approx 80 - 85$ K and mounted at an angle to the beam axis is studied. It is found that the excited molecules pass much more readily through the cone than the unexcited (vibrationally cold) molecules. This opens the possibility for studying the processes of energy transfer and redistribution over a cold surface covered by molecular (cluster) layers, and for separating excited and unexcited molecules in a beam.**

Keywords: *multiphoton IR excitation of molecules, interaction of molecules with a surface, physical adsorption and desorption, laser selection of molecules.*

1. Introduction

Atomic and molecular processes at a surface, including those induced by laser radiation, are being studied intensely in many laboratories [1 – 14]. This is due to fundamental as well as practical aspects of quite complex and diverse phenomena occurring during the interaction of atoms and molecules with a surface (energy transfer, redistribution, and relaxation, chemical reactions at a surface, heterogeneous catalysis, etching, sputtering of films, condensation and formation of mist and smog, etc.)

In addition, the processes of interaction (trapping, energy transfer, adsorption, desorption, and reflection) of vibrationally excited and unexcited molecules with molecular (cluster) layers condensed on a cold surface are also of considerable interest. The results of such investigations are important not only for understanding the microscopic processes occurring at a surface, but also for the application of these processes in actual practice, e.g., for laser selection of molecules or for directed photochemical reactions [3, 4, 6, 10, 13]. So far, such processes have been studied insufficiently. However, we can indicate a number of results which have been well-established in experiments on studying the interaction of atoms and molecules with a surface (see, for example, [3, 12]).

First, during physical adsorption of atoms or molecules at a clean cold surface or one covered by particles, there is no potential barrier for the capture of a particle in most cases [3, 12]. Therefore, the capture probability decreases with increasing energy E_i of an incident atom or molecule. This is due to the fact that for capturing to take place in the case of high energies E_i, a considerable part of the incident energy must be lost [3, 12]. In particular, trapping in a potential with the effective potential well of depth ε will occur only if the part of the incident energy lost in collisions exceeds the quantity $E_i/(E_i + \varepsilon)$ [3]. Second, the lifetime of an atom or a molecule adsorbed at a surface is determined by the desorption energy E_{des} and the surface temperature T_s [12]: $\tau = \tau_0 \exp(E_{des}/kT_s)$, where τ_0 is a preexponential factor which is of the same order of magnitude as the period of molecular vibrations of particles ($\tau_0 \sim 10^{-11} - 10^{-13}$ s), and k is the Boltzmann constant. Finally, the probability p of desorption of a molecule from a surface depends on the binding energy E_b of the molecule with the surface and on the surface temperature T_s: $p \sim \exp(-E_b/kT_s)$ [3, 12].

For a surface covered by a layer of molecules, E_b is the energy of binding with molecules at the surface or binding energy of molecules in a cluster. Hence, if the total energy of a molecule in a beam incident on a cold surface covered by molecular (cluster) layers is lower than the binding energy of molecules in clusters, as well as the binding energy of a molecule with the surface, it will be captured by the interaction potential and will remain at the surface. If, however, the total energy of the molecule is higher than the above quantities, it can be reflected from the surface. This, however, is just a simplified version of the model. As a result of rapid relaxation processes occurring during interaction of molecules with the surface [1 – 3, 12], the molecular energy may be lost partially or completely, or redistributed between various degrees of freedom. As a result, the potential barrier will not be overcome and the molecule will also be captured at the surface.

However, the higher the energy of a molecule, the longer the time required for its complete relaxation [1 – 3]. Hence, the coefficient of reflection of molecules from the surface (or the fraction of reflected molecules) will depend on the energy of molecules as well as its distribution between various degrees of freedom [3, 14]. A fairly high energy (comparable with the dissociation energy of a molecule) can be imparted to the vibrational degrees of freedom due to multiphoton IR absorption [15 – 17]. Therefore, it can be assumed that the probability of reflection of highly vibrationally excited

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Received 22 May 2006
Kvantovaya Elektronika **36** (9) 889 – 894 (2006)
Translated by Ram Wadhwa

molecules from the molecular (cluster) layers condensed at the surface will be much higher than the reflection probability for vibrationally cold (unexcited) molecules.

We showed recently [18] that SF_6 molecules excited to high vibrational states (with energy $E_v \geqslant 0.5-2.0$ eV) have a much higher probability than unexcited molecules of passing through a multichannel metal plate cooled to 80–85 K and installed at an angle to the beam axis. It was also found in these experiments that CF_3I molecules exhibit the same behaviour. However, the process involving the participation of CF_3I molecules was not studied by us in detail. Nevertheless, the results of such investigations are of considerable interest on account of the potentialities of using this process for selection of excited and unexcited molecules, especially in laser isotope separation. In this connection, it should be remarked that at the initial stages of investigation of selective IR dissociation of molecules, it is the CF_3I molecule that was considered as a possible candidate for laser separation of carbon isotopes (see, for example, [15–17] and the literature cited therein, as well as [19]).

The processes of multiphoton IR excitation and dissociation of CF_3I molecules have been studied quite extensively [15–17, 20, 21], especially in molecular beams [16, 17, 22–24] and flows [25–31]. IR absorption spectra of $^{12}CF_3I$ and $^{13}CF_3I$ molecules have been studied in detail [32]. Such a molecule is characterised by a comparatively low dissociation energy (about 2.3 eV [33]) and is desorbed quite effectively for moderate energy densities of IR radiation (higher than 2 J cm^{-2}) [21, 25–31]. The thermal chemistry of CF_3I molecules at a solid surface has also been studied in detail, including processes of adsorption and desorption (see, for example, [34] and the literature cited therein). The results of these investigations have a direct impact on our experimental investigations. For example, it is mentioned in [34] that desorption of CF_3I molecules adsorbed at a cold Ag(111) surface covered by the same molecules occurs (upon an increase in temperature) without dissociation of molecules.

In the present research, we have studied thoroughly the passage of vibrationally excited and unexcited CF_3I molecules through a cooled hollow converging cone. The use of a cone makes it possible to increase the number of molecules (compared to the multichannel plate) interacting with the surface, and hence to increase the efficiency of the process. Moreover, experiments with a cone reveal certain characteristic features of the process which cannot be determined in experiments with a multichannel plate [like finding the fraction of molecules incident on the cone and those passing through it (see Section 4 and Fig. 3)]. We found that molecules excited to high vibrational states (with an energy $E_v \geqslant 0.3-1.5$ eV) pass much more efficiently through a cone than unexcited (vibrationally cold) molecules. Below, we describe in detail the experimental setup and the measuring technique used by us, and the first results of our investigations.

2. Experiment and measuring technique

Figure 1 illustrates the principle of the method. A high-intensity (more than 10^{20} mol sr^{-1} s^{-1}) wide-aperture (divergence $\omega \approx 0.2$ sr) pulsed molecular beam was incident on a liquid-nitrogen-cooled copper cold finger and a hollow converging truncated copper cone attached to it. The diameters of the input and output apertures of the cone were 9 and 4 mm respectively, and the length of the cone was 25 mm. The cold finger had an aperture in the form of a converging cone with input and output apertures of 11.8 and 9 mm respectively. The cold finger was 8-mm thick. The cone temperature T_s measured by a thermocouple was 80–85 K. The separation from the nozzle cut to the input aperture of the cone was 75 mm. In order to exclude the possibility of the cone operation in the 'transparent' regime, it was tilted through an angle of $\alpha \geqslant 20°$ to the incident beam axis. The angle at which the cone became 'opaque' for the incident beam was determined by the diameter of the input and output apertures of the cone, the angle of its convergence, as well as the distance of the nozzle aperture from the input aperture of the cone. The input aperture of the cone can be treated as the input aperture of the cold finger (see Fig. 1). Taking this into account, the total length of the cone aperture was 33 mm, while the angle at which the cone became 'opaque' was $\sim 19.5°$.

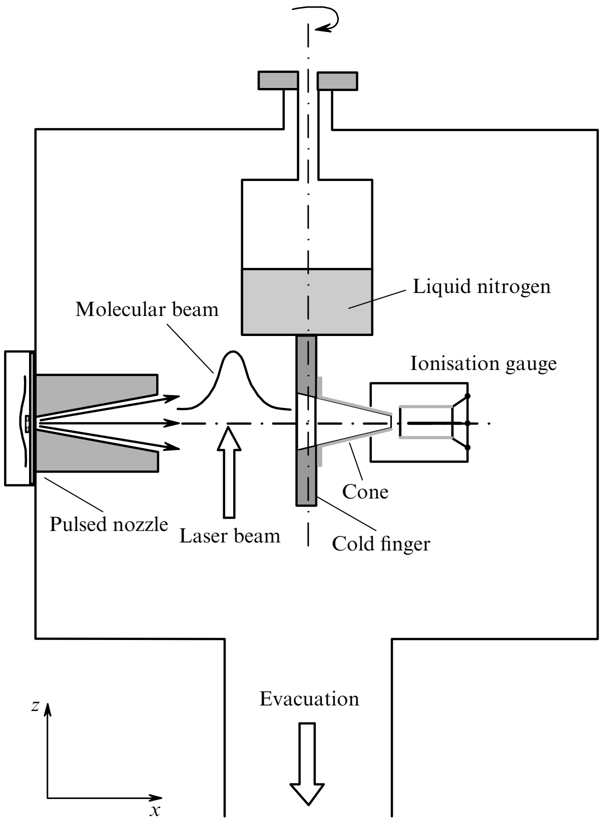

Figure 1. Scheme of the experimental setup.

A molecular beam was obtained by using a pulsed nozzle of the current-loop type [35] with an orifice of diameter 0.75 mm. Depending on the gas composition and pressure over the nozzle, the nozzle opening time was $\sim 70-100$ μs (at half-height). The pressure varied in the range 0.1–6 atm. The nozzle was cut in the form of a cone with a total cone angle of 26°, the length of the cone being 30 mm. The vacuum chamber in which the molecular beam was formed was evacuated by a diffusion pump to a pressure of $\sim 3\times10^{-6}$ Torr. The number of molecules flowing out of the nozzle during one pulse was determined by the gas pressure over the nozzle and varied from $\sim 8\times10^{14}$

to $\sim 1 \times 10^{17}$ mol pulse^{-1}. The method of measurement of the number of molecules in a pulse is described in detail in [16, 17, 25, 36]. The nozzle could operate in a single pulse regime or at a pulse repetition rate of up to 1 Hz.

Molecules were excited to vibrational states by a high-power tunable pulsed CO_2 laser ($10^6 - 10^7$ W cm^{-2}). The pulse energy was 3 J. The laser pulse consisted of a peak with the full width at half-maximum of $\sim$ 100 ns and a tail of duration $\sim$ 0.6 μs containing $\sim$ 50 % of the pulse energy. The laser beam crossed the molecular beam at the right angle at a distance of about 1.5 – 2 cm from the output aperture of the cone. The laser-spot area in the excitation region was 10×10 mm. In most of the experiments we used a two-pass scheme for exciting molecules in the beam. In this case, the laser beam intersecting the molecular beam at a small angle was reflected in the backward direction, which allowed excitation of nearly double the number of molecules in the beam.

It should be emphasised once again that in the experiments described here, we are dealing with the interaction of highly vibrationally excited molecules and unexcited molecules with molecular (cluster) layers condensed on a cold surface. Molecular layers on the surface of the cone walls are formed due to condensation of vibrationally cold molecules of the incident beam on these walls. Note that when the surface contains a large number of molecules (more than one layer, no less than 10^{14} mol cm^{-2}), they can exist in the form of clusters [37]. Because we used high-intensity pulsed molecular beams in our experiments, a great number of molecular layers (no less than 10 – 20) could be formed on the cold surface of cone walls even upon incidence of only one pulse or only its leading part that was not exposed to laser radiation (see Fig. 1).

Molecules passing through a cone and molecules in the initial beam were detected with a PMI-2 ionisation pressure gauge, which was installed in such a way that the molecules passing through the cone fell directly on the gauge. The cone and the gauge could be rotated together around a vertical axis (see Fig. 1), thus making it possible to vary the angle α of incidence of the beam on the cone, and hence the transparency of the cone. Because the signal from the ionisation gauge is proportional to pressure or the number of molecules (and is independent of their vibrational energy), this method makes it possible to find the relative number of molecules passing through the cone without laser excitation as well as upon excitation by a laser beam. The signal from the ionisation gauge was fed to a VIT-2 pressure meter and an N307/1 recorder.

Note that we also used the pyroelectric detection technique for detecting the molecules of the initial beam and the molecules passing through the cone [16, 17, 38 – 40]. In this case, the sensitivity of the method was enhanced by using a second CO_2 laser pulse for exciting the molecules passing through the cone. This made it possible to detect reliably the passage of molecules through the cone and to determine the fraction of molecules passing through the cone. The both methods used by us gave nearly the same results. The data presented below were obtained with an ionisation gauge.

3. Results and discussion

We studied the passage of CF_3I molecules through a cooled cone without and upon excitation by a laser pulse. It was found (Fig. 2) that the probability of passage of vibrationally excited molecules through the cone was much higher than that for unexcited molecules. Figure 3 shows the dependence of an ionic signal induced by unexcited CF_3I molecules passing through the cone on the angle of incidence α of a molecular beam at the cone (angle $\alpha = 0$ corresponds to the case when the beam propagates along the cone axis). The figure shows the results for a warm [$T_s \approx 295$ K, curve (*1*)] and a cooled [$T_s \approx 80 - 85$ K, curve (*2*)] cones. One can see (see Fig. 3a) that the signal for the cooled cone and $\alpha = 0$ is 7.5 times weaker than for the warm cone. This ratio of signals is just slightly lower than the ratio R of the areas of the input and output apertures of the cone: $R = S_{\text{in}}/S_{\text{out}} \approx 9$. This means that, first, the main part of CF_3I molecules incident on the cold walls of the cone are captured by them. Only molecules propagating in a solid angle determined by the size of the output aperture of the nozzle as well as a small part of molecules reflected by the cold walls of the cone can pass without hindrance through the cone. Second, nearly all the molecules incident at the input aperture at $T_s \approx 295$ K and $\alpha = 0$ pass through the cone. However, it can be seen from Fig. 3b [cf. curves (*1*) and (*3*)] that upon an increase in angle α, not all the molecules entering the cone pass through it even at $T_s \approx 295$ K. Some of the molecules are reflected at the cone walls in the opposite direction. However, the fraction of the molecules passing through the cone is quite high (no less than 55 % for $\alpha = 30°$).

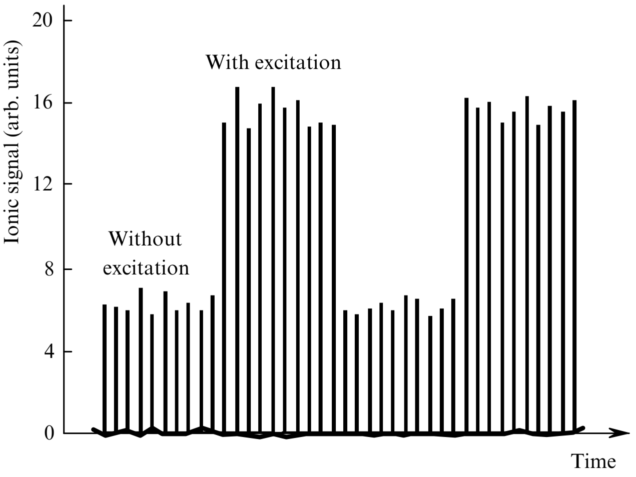

Figure 2. Diagram illustrating the passage through a converging cone cooled to $T_s \approx 80 - 85$ K of a beam of unexcited CF_3I molecules and molecules excited vibrationally by a laser pulse. The angle of incidence α of the molecular beam at the cone is 32.5°, the radiation excitation frequency $\nu = 1071.88$ cm^{-1} [9R(10) line of the CO_2 laser], the radiation energy density $\Phi = 0.8$ J cm^{-2}, and the pressure p of CF_3I over the nozzle is 2 atm.

The situation is entirely different in the case of a cooled cone (Fig. 3b). When the angle of rotation α of the cone achieves $\sim 20°$ and the cone is no longer 'transparent' for the incident particles (under the conditions of our experiments, $\alpha \approx 19.5°$), the probability (efficiency) of passage of CF_3I molecules through the cone decreases sharply. For $\alpha \geqslant 25°$, the fraction of molecules passing through the cone is quite small (less than 10 %). However, the efficiency of passage of molecules through the cooled cone increases

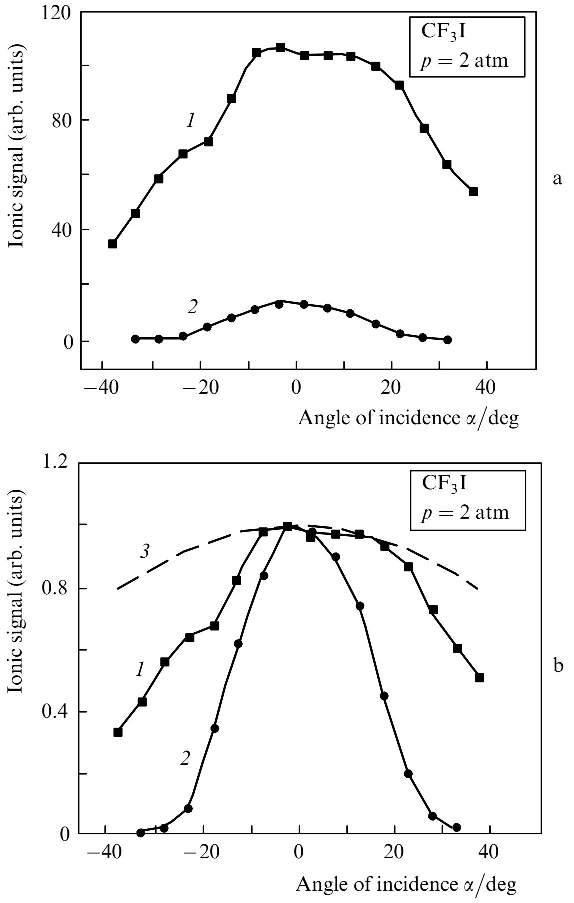

Figure 3. Dependence of the intensity of ionic signals induced by CF$_3$I molecules passing through the cone on the angle of incidence α. The signals were obtained for warm [curve (*1*)] and cooled [curve (*2*)] cones. Figure 3b shows the same data, but the maximum value of the signals has been normalised to unity for better visualisation. Curve (*3*) ($\cos\alpha$) is presented for comparison.

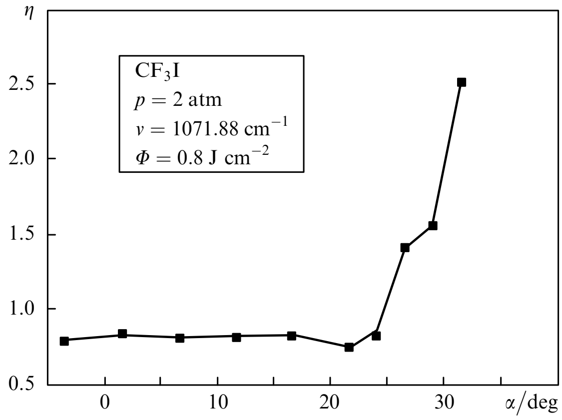

Figure 4. The ratio $\eta = I_{\rm las}/I_0$ of the intensities of signals induced by CF$_3$I molecules passing through the cone for vibrationally excited and unexcited molecules, as a function of the angle of incidence α of the molecular beam on the cone. The experimental conditions are the same as in Fig. 2.

significantly, when the molecules in the beam are excited by high-intensity laser pulses (see Fig. 2).

Figure 4 shows the ratio $\eta = I_{\rm las}/I_0$ of ionic signals induced by the CF$_3$I molecules passed through the cone in the case of molecular beam excitation ($I_{\rm las}$) and without excitation (I_0) as a function of the angle α. One can see that for $\alpha \geqslant 22°$, this ratio increases with the angle and for $\alpha = 32.5°$ we have $\eta \approx 2.6$. For small angles α, the value of η is slightly lower than unity due to the fact that for the exciting laser radiation energy density in our experiments, a small fraction of molecules were dissociated and the resulting fragments 'escaped' from the beam (see also Fig. 5). Note that in our experiments, about half the incident beam molecules were exposed to laser radiation. Hence, considering the fact that nearly all the molecules in the exposed volume were excited to high vibrational states for the pump energies used in our experiments [16, 18, 25, 40], the probability of passage of highly excited molecules ($p_{\rm las}$) for $\eta \approx 2.6$ is about 4.2 times higher than the probability p_0 of passage of unexcited molecules ($\frac{1}{2}p_0 + \frac{1}{2}p_{\rm las} = 2.6p_0$, which leads to the ratio $p_{\rm las}/p_0 = 4.2$).

We also found that the efficiency of passage of molecules through a cooled cone depends significantly on frequency ν as well as the energy density Φ of the exciting laser radiation (Fig. 5). This means that the probability of reflection of molecules from a cold surface depends strongly on their vibrational energy. For example, the maximum signal induced by the molecules passing through the cone was observed when CF$_3$I molecules were excited at frequencies of 9R(8)−9R(16) lines of the generation band of 9.6-μm CO$_2$ laser, i.e., in the frequency range 1070−1075 cm^{-1}, where the maximum absorption of CF$_3$I is observed in the molecular beam [16, 17, 25, 40]. For example, the average laser energy absorbed per CF$_3$I molecule is no less than 1−1.5 eV for an energy density of 1.5 J cm^{-2} and no less than 0.3 eV for an energy density of 0.3 J cm^{-2} [16, 17, 25, 40]. In our experiments, the translational energy $E_{\rm tr}$ of CF$_3$I molecules in the beam was ~ 0.18 eV [16, 17, 41, 42]. The decrease in the percentage of transmitted molecules with increasing the excitation energy density for $\Phi \geqslant 0.5 - 1.0$ J cm^{-2} (Fig. 5) is due to the dissociation of molecules and escape of the formed fragments from the beam.

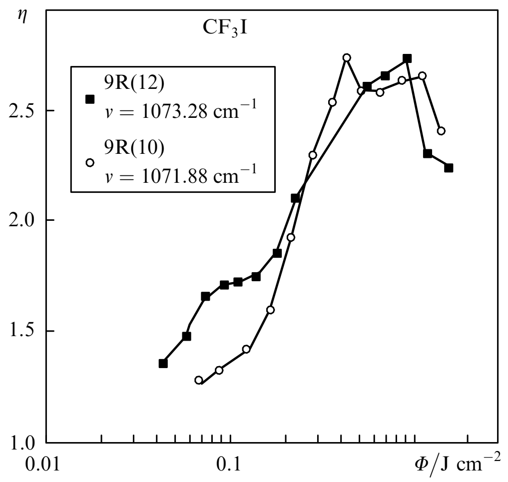

Figure 5. The ratio $\eta = I_{\rm las}/I_0$ of the intensities of signals induced by CF$_3$I molecules passing through the cone for vibrationally excited and unexcited molecules, as a function of the energy density of the exciting laser radiation for two frequencies. The experimental conditions are the same as in Fig. 2.

Note that similar results, which show an increase in the probability of passage of vibrationally excited molecules through the cone, were also observed by us with an SF_6 molecular beam. The increase in the probability of passage of vibrationally excited CF_3I and SF_6 molecules through the cone is due to the fact that the energy of excitated molecules is much higher than the binding energy of molecules in clusters (for example, this value for SF_6 is ~ 0.29 eV [37]). As a result, vibrationally excited molecules are reflected with a higher probability than unexcited molecules from a surface covered by molecules.

As mentioned above, to our knowledge, the interaction of molecules excited vibrationally to high energies with molecular (cluster) layers condensed on a cold surface has not been studied so far. In earlier paper [43], however, the role of translational and vibrational energy of SF_6 molecules in a continuous beam was studied during their reflection from a cold surface. The translational and vibrational energy of SF_6 molecules was varied (over a limited range) by heating the nozzle. It was found that the reflection coefficient for vibrationally excited molecules was (several times) larger than for unexcited molecules only if the translational energy of molecules was low (no more than 0.04 eV). For translational energy values higher than 0.15 eV, no difference was observed in the reflectivities of excited and unexcited molecules. The experiments in [43] were carried out at a surface temperature of about 50 K, while the total fraction of molecules reflected from the surface was less than 1 %.

Note also that investigations in [43] were performed under conditions when the molecules had a small store of vibrational energy (less than 0.12 eV) since the excitation of molecules by a cw CO_2 laser or by heating the nozzle did not lead to population of higher vibrational states. As a result, the effect of vibrational excitation of molecules on the investigated processes was insignificant. Results of our experiments (see also [18]) differ from those presented in [43] in that our investigations were carried out with highly excited molecules with a vibrational energy exceeding $0.3-1.5$ eV. For such high energies, relaxation of vibrational excitation requires a large number of collisions and hence a longer time. Another basic difference lies in that the vibrational energy of molecules in our experiments was much higher than the binding energy of molecules in clusters and the binding energy of molecules with the surface ($0.2-0.3$ eV). Probably this is why we were able to detect a large difference in the probabilities of passage of excited and unexcited molecules through a cone. Under conditions when $\alpha = 30^\circ$ and $\eta \geqslant 2$ (see Fig. 4), about 5 % – 7 % of the molecules incident at the cone passed through it.

4. Conclusions

We have shown that CF_3I molecules excited in a beam by high-intensity IR laser radiation to high vibrational states (with an energy $E_v \geqslant 0.3-1.5$ eV) pass much more efficiently through a hollow converging cone cooled to $T_s \approx 80-85$ K than the unexcited molecules. It is found that the probability of passage of molecules through a cone depends to a considerable extent on the energy density and the frequency of the exciting laser pulse. The method proposed in this work can be probably used to study complex processes of transfer and redistribution of energy during interaction of highly excited molecules with the surface on which molecules are condensed, and to perform the isotopic (component) selection of molecules in beams.

Acknowledgements. The authors are grateful to V.M. Apatin and V.N. Lokhman for their help and for fruitful discussions. This work was supported by the Russian Foundation for Basic Research (Grant Nos 03-02-17067 and 06-02-16634).

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