Acceleration of neutral molecular beams by an IR laser

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A method is proposed for accelerating neutral molecular beams. It involves exciting the molecules with intense IR laser light in the zone of gasdynamic expansion at the exit from a nozzle. The results of a corresponding study are reported. This method can produce intense molecular beams with a kinetic energy >1 eV. It can be combined with aerodynamic acceleration. © *1995 American Institute of Physics.*

1. Intense molecular beams with kinetic energies from 1 to several eV are required in various fields of fundamental and applied research (in research on chemical reactions with energy barriers, in the interaction of molecules with surfaces, etc.).[1] There are several ways to solve this problem.[2,3] The various possibilities can be classified on the basis of the process which underlies the control of the energy of the molecules: 1) an electrostatic process in which ion beams are neutralized; 2) a thermodynamic process in which molecular beams are selected from freely expanding supersonic jets. In the first of these categories, the kinetic energy of the molecules can be controlled by varying the voltage on electrodes in the beam path. In the second approach, the kinetic energy is determined by the gas temperature before expansion through the nozzle, T_0:

$$\tfrac{1}{2}mv^2=\frac{\gamma}{\gamma-1}\,k(T_0-T). \tag{1}$$

Here v is the steady-state flow velocity, m is the mass of a molecule, $\gamma=C_p/C_v$ is the ratio of specific heats of the expanding gas, k is the Boltzmann constant, and T is the steady-state temperature.

At room temperature, the kinetic energy of the molecules thus cannot be increased unless the gas of interest is diluted with a lighter "carrier" gas.[4,5] That method is not particularly effective when the ratio of the masses of the gas of interest and the carrier is small. That method can be combined with a heating of the nozzle to $\simeq 3000$ K. A system of this sort makes it possible to accelerate (for example) argon atoms diluted with helium to several eV (Ref. 6). That approach again is of less than universal applicability, since at high temperatures there may be dissociation of molecules, damage to the nozzle material, and other problems. A cw laser discharge inside the nozzle, just in front of the exit aperture, was proposed in Ref. 7 as a way to solve this problem. The discharge would be ignited by a pulsed laser or electric spark and sustained by a cw CO_2 laser. Obviously, that method is still of less than universal applicability, and realizing it in practice is a rather complicated technical problem.

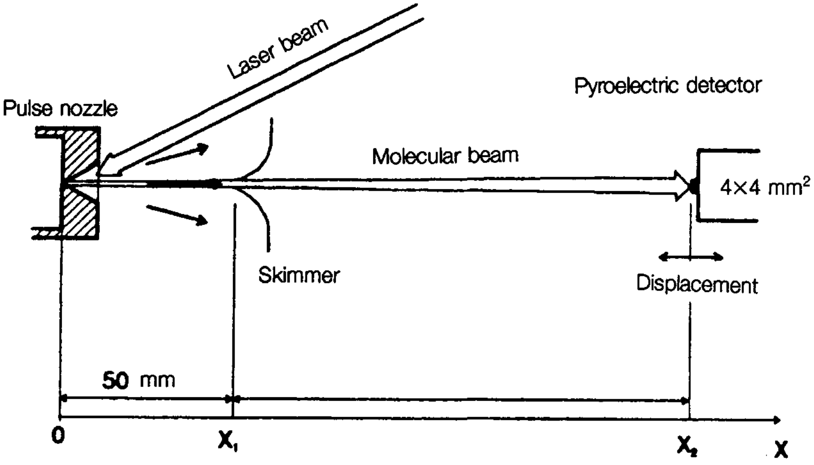

FIG. 1. Schematic diagram of the experimental apparatus.

In this letter we describe a method for accelerating neutral molecular beams which is based on excitation of molecules by IR laser light in a zone of gasdynamic expansion. Here is the basic idea of the method: Molecules leaving a nozzle are excited by intense, resonant IR laser light in the zone of gasdynamic expansion just beyond the exit from a nozzle. The IR absorption of the molecules leads to a significant increase in their internal energy (primarily vibrational). At the same time, the internal energy decreases, and the kinetic energy of the molecules simultaneously increases, as the result of vibrational–translational (V–T) relaxation.

2. Figure 1 is a schematic diagram of the experimental apparatus. The apparatus is described in detail in Refs. 8 and 9; here we will describe it only briefly. A pulsed nozzle of the "current loop" type,[10] operating at room temperature, was used in the experiments. The diameter of the nozzle aperture was 0.75 mm. The opening time was $\simeq 60$ μs (at half-maximum). The nozzle was made of a Duralumin. The end of the nozzle was a cone with a total vertex angle of 60°. The length of this cone was 15 mm. The vacuum chamber in which the molecular beam was formed was evacuated to $\simeq 1\times 10^{-6}$ torr. The nozzle operated at a frequency of 0.2 Hz. The molecular beam was separated from the jet by means of a conical diaphragm (skimmer) with an aperture 1.5 mm in diameter. This skimmer was positioned 50 mm away from the end of the nozzle.

The molecules were excited[8,9] by a pulsed TEA CO_2 laser, which was frequency-tuned by means of a diffraction grating. This laser generated pulses with an energy up to 3 J. The laser energy was reduced to $\simeq 0.1$ J, in order to prevent optical breakdown within the nozzle, by singling out the TEM_{00} mode and by using additional attenuation with CaF_2 plates. The laser light was directed into the zone of gasdynamic expansion without focusing.

The molecular beam was detected[8,9] with an cooled pyroelectric detector with a time resolution $\simeq 3$–5 μs (Ref. 11). This detector could be moved along the beam axis by a mechanical device. This approach made it possible to record time-of-flight spectra of the molecules at various points along the beam axis[9] and also to directly measure the most probable velocity of the molecules (at the maximum of the time-of-flight distribution). The signal from the pyroelectric detector was amplified (by a factor of 100) and fed to the input of an S9-16 digital storage oscilloscope.

Without preliminary excitation of the molecules, the signal from the detector is proportional to the quantity

$$S_0 \sim nv(E_a + E + mv^2/2) \sim nvE_0, \tag{2}$$

where n is the number density of molecules at the surface of the detector, v and m are the velocity and mass of a molecule, E is the energy of the molecule (this is the sum of the vibrational, rotational, and "local" translational energies), and E_0 is the total energy (the sum inside the parentheses). When the molecules in the beam are excited by a laser pulse, the signal is proportional to the quantity[8,9]

$$S_L \sim nv(E_0 + E_{ab}), \tag{3}$$

where E_{ab} is the energy absorbed from the laser field by a molecule.

If the molecules in the beam are excited at a distance from the nozzle large enough ($X > 50$ mm) that there are essentially no collisions or $V-T$ relaxation, the velocity of the excited molecules does not differ from that of the unexcited molecules.[8,9] If, in contrast, the molecules are excited in the zone of gasdynamic expansion, where the collision rate is high, then the absorbed energy is converted completely or partially into translational degrees of freedom as a result of $V-T$ relaxation, with the result that there is an acceleration of the molecules, including those which do not absorb IR light.

3. In the experiments, we measured time-of-flight spectra of the molecules in the beam at various distances from the nozzle, and we determined the most probable velocity of the molecules in beams which were and were not accelerated. In the experiments we used the molecules SF_6, CF_3I, NH_3, and CF_2HCl, both with and without carriers (H_2, D_2, N_2, Ar, and CH_4). Figure 2 shows signals from the detector (the time-of-flight spectra of the SF_6 molecules) without laser acceleration (a) and with it (b, c). The molecules were excited at the 10P(20) line ($944.2\ \mathrm{cm}^{-1}$) of a CO_2 laser. This line makes a good resonance with the ν_3 vibration of the molecule.[8,12] In the case in Fig. 2b, the time interval (delay) between the pulses triggering the nozzle and the CO_2 laser was set at a value ($\tau_d = 120\ \mu s$) such that all the molecules in the beam would be accelerated. In the case in Fig. 2c, this delay was shorter ($\tau_d = 60\ \mu s$), so only the molecules which were the first to leave the nozzle would be accelerated; the rest would not be accelerated. When the delay was instead increased ($\tau_d = 180\ \mu s$), and the laser pulse excited the last molecules to leave the nozzle, the accelerated molecules overtook the unaccelerated molecules of the beam.

The most probable velocity of the SF_6 molecules in the case without laser acceleration was $v_0 = 470 \pm 10$ m/s. This velocity corresponds to a kinetic energy $E_{\mathrm{kin}} \simeq 0.17$ eV. The velocity of the accelerated molecules was $v_L = 815 \pm 15$ m/s, which corresponded to $E_{\mathrm{kin}}^L \simeq 0.51$ eV. In combination with aerodynamic acceleration of the SF_6 molecules with methane ($SF_6:CH_4 = 1:10$, $p_\Sigma = 1$ atm), we obtained $v_0 \simeq 1000$ m/s and $v_L \simeq 1200$ m/s. This result corresponds to a kinetic energy $E_{\mathrm{kin}}^L \simeq 1.0$ eV of the SF_6 molecules.

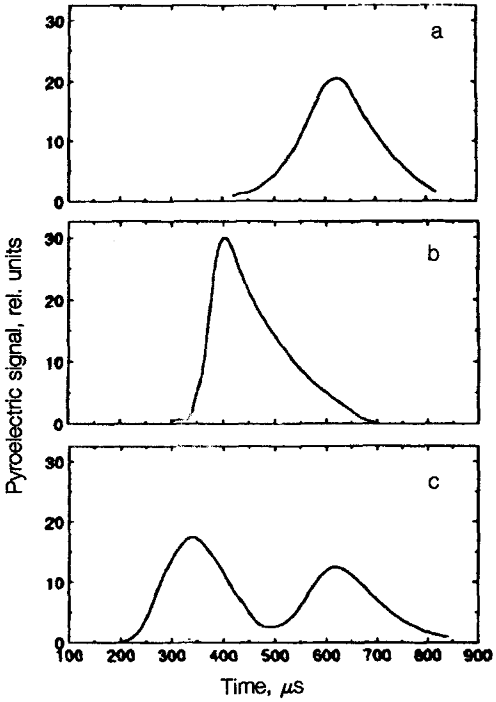

FIG. 2. Time-of-flight spectra of SF_6 molecules without laser acceleration (a) and with laser acceleration (b, c). In case b, all the molecules in the beam are accelerated; in case c, only those molecules which are the first to leave the nozzle are accelerated. The distance from the nozzle to the detector is 25 cm. The SF_6 pressure in the nozzle is 4 atm. The energy of the CO_2 laser is either (b) 0.1 J or (c) 0.05 J. The 10P(20) line was used.

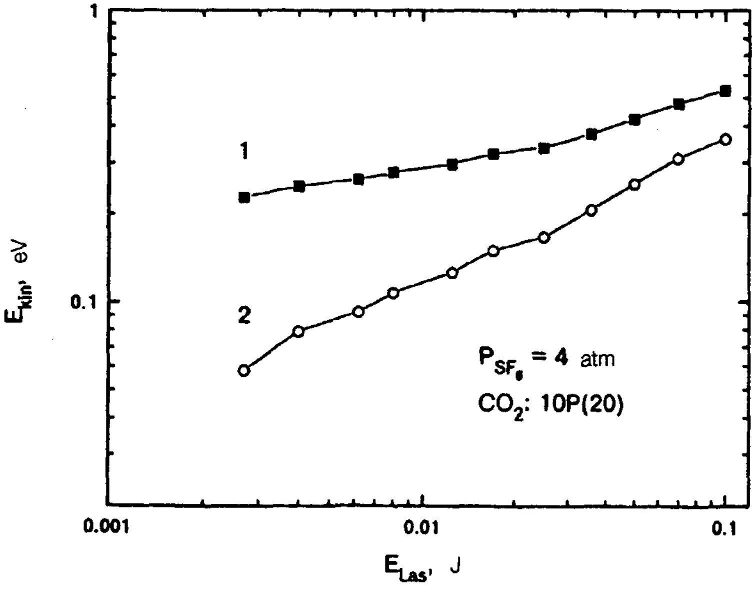

FIG. 3. Kinetic energy of the accelerated SF_6 molecules versus the energy of the exciting pulse from the CO_2 laser. 1—The total kinetic energy of the SF_6 molecules in the beam; 2—the kinetic energy induced by the laser. The SF_6 pressure in the nozzle is 4 atm; the laser line is 10P(20).

In some similar experiments with CF_3I [$p_0 = 1$ atm, excitation in the ν_1 vibrational band of the molecule by the 9R(12) line of the CO_2 laser, at 1073 cm^{-1}; Ref. 13], the velocity of the molecules in the absence of the laser acceleration was $v_0 = 415 \pm 10$ m/s ($E_{kin} = 0.18$ eV), while that in the case with acceleration was $v_L = 845 \pm 15$ m/s. This result corresponds to a kinetic energy $E^L_{kin} \simeq 0.74$ eV. In combination with aerodynamic acceleration of CF_3I in a mixture with methane ($CF_3I{:}CH_4 = 1{:}15$, $p_\Sigma = 1.3$ atm), the most probable velocity in the absence of laser acceleration was $v_0 = 815 \pm 15$ m/s, while that with laser acceleration was $v_L = 1065 \pm 20$ m/s. This result corresponds to a kinetic energy $E^L_{kin} \approx 1.2$ eV of the CF_3I molecules.

Figure 3 shows the kinetic energy of the SF_6 molecules versus the energy of the exciting laser pulse. Curve 1 shows the total kinetic energy of the molecules, and curve 2 shows the energy induced by the laser. We see that, over the range studied, the energy induced by the laser increases with increasing energy of the exciting pulse, E_p, in accordance with $E^L_{kin} \propto E_p^{1/2}$. There is no saturation here. The behavior is almost the same as that of the absorption of SF_6 (Refs. 8 and 12). One might thus suggest that molecular beams with a kinetic energy > 1 eV could be produced by raising the energy of the exciting pulse (this would be a simple matter with a nozzle without a cone[9]) and by raising the gas pressure in the nozzle. The peak intensity of the accelerated molecular beams in this case would be $> 10^{21}$ molecules/(sr·s).

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[1] *Atomic and Molecular Beam Methods*, ed. by G. Scoles (Oxford University Press, New York, 1988).
[2] H. Pauli, in *Atomic Molecular Beam Methods*, ed. by G. Scoles (Oxford University Press, New York, 1988).
[3] J. M. Girard, A. Lebehot, and R. Comparque, J. Phys. D **26**, 1382 (1993).
[4] E. W. Becker and W. Henkes, Z. Phys. **146**, 320 (1956).
[5] K. Kolodney and A. Amirav, Chem. Phys. **82**, 269 (1983).
[6] R. Comparque, A. Lebehot, J. C. Lemonnier, and D. Marette, *Rarefied Gas Dynamics*, ed. by S. S. Fisher (AIAA, New York, 1980), p. 823.
[7] P. Asselin, C. Meis, L. Lebehot *et al.*, *Rarefied Gas Dynamics*, ed. by A. E. Beylich (VCH, Weinheim, 1991), p. 1466.
[8] V. M. Apatin and G. N. Makarov, Zh. Eksp. Teor. Fiz. **84**, 15 (1983) [Sov. Phys. JETP **57**, 8 (1983)].
[9] V. M. Apatin, L. M. Dorozhkin, G. N. Makarov, and G. M. Pleshkov, Appl. Phys. B **29**, 273 (1982).
[10] W. R. Gentry and C. F. Giese, Rev. Sci. Instrum. **49**, 595 (1978).
[11] R. V. Ambartzumian, L. M. Dorozhkin, G. N. Makarov *et al.*, Appl. Phys. **22**, 409 (1980).
[12] R. V. Ambartsumyan, Yu. A. Gorokhov, V. S. Letokhov, and G. N. Makarov, Zh. Eksp. Teor. Fiz. **69**, 1956 (1975) [Sov. Phys. JETP **42**, 993 (1975)].
[13] V. M. Apatin and G. N. Makarov, Kvant. Elektron. (Moscow) **10**, 1435 (1983) [Sov. J. Quantum Electron. **13**, 932 (1983)].

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