

# Selection of excited molecules by an inhomogeneous electric field

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(Submitted June 7, 1975)

*Pis'ma Zh. Eksp. Teor. Fiz.* **22**, No. 3, 165-168 (August 5, 1975)

A method of selecting vibrationally excited molecules by an inhomogeneous electric field has been proposed in [1] and is based on the difference between the deflection of the excited and unexcited molecules by the field. It is also indicated that the method can be realized for nonpolar symmetrical molecules. However, in view of the absence of a first-order Stark effect for all nonpolar molecules of the symmetric- and spherical-top type (with the exception of the  $E$  states of tetrahedral molecules [2]) it is advisable to search for other objects for which the method can be realized.

The dipole moment of nonpolar molecules is exactly equal to zero only in the ground vibrational-rotational state. In the ground vibrational state (and also in all the excited states), owing to the centrifugal distortion, a dipole moment  $\sim \theta J^2$  is produced, with  $\theta < 10^{-4}$  D. [2-5] In some degenerate vibrational states, owing to the mechanical and electrooptical anharmonicity, there is a constant dipole moment, given for molecules with symmetry  $T_d$  in a state of type  $F_2$  by the formula [6,11]

$$\langle \mu_t \rangle = \frac{1}{2\omega_t} \left\{ \left( \frac{\partial^2 \mu_x}{\partial Q_x \partial Q_y} \right)_e - \sum_i \phi_{t_x t_y i} \left( \frac{\partial \mu_x}{\partial Q_x} \right)_e \frac{1}{\omega_i} \right\}, \quad (1)$$

where  $\omega_t$  is the frequency of the triply degenerate oscillation  $Q_t$ ,  $\phi_{t_x t_y i} = \partial^3 u / (\partial Q_{t_x} \partial Q_{t_y} \partial Q_i)$  are the anharmonicity coefficients. For the  $\nu_3$  state of  $\text{CH}_4$  we have  $\langle \mu_3 \rangle \approx 0.02$  D, [9] while for heavier molecules  $\langle \mu_t \rangle < 0.01$  D [1]. In addition, a field with  $E \sim 10^9$  V/cm induces in a molecule a dipole moment  $\alpha E$  ( $\sim \langle \mu_t \rangle$ ), which, owing to the weak dependence on the vibrational-rotational state,

violates the selectivity condition.

Thus, owing to the absence of a linear Stark effect (with rare exceptions), owing to the smallness of the dipole moment of the excited vibrational state, and owing to the dependence of the centrifugal dipole moment and of the nonselective polarization of the molecule on  $J$ , the method of selecting excited nonpolar molecules of quasirigid molecules by an electric field is technically difficult to realize. This method can be realized, however, for other classes of molecules, above all polar nonrigid molecules.

From the results of experiments on the focusing of molecular beams by an electrostatic field it is known that molecules with a dipole moment  $\mu > 0.02$  D in the presence of a linear Stark effect and molecules with  $(\mu/\Delta^{1/2}) > 0.1$  D-cm $^{1/2}$ , in the presence of a quadratic Stark effect are easily focused in a field with  $V_{\text{max}} \sim 35$  V ( $\Delta$  is the interval between levels coupled by a Stark matrix element). [11] We can indicate many molecules for which these conditions are satisfied (quasilinear molecules, quasiplanar four- and five-member cyclic molecules, molecules with internal rotation, etc. [12]), but from the practical point of view the most interesting is the ammonia molecule. The vibrational-rotational states of ammonia consist of inversion doublets, for which the Stark shift is given by the approximate formula

$$\mathcal{W}_i = \mathcal{W}_{JK} \pm \left\{ \left( \frac{\Delta}{2} \right)^2 + \left[ \frac{\mu E K M}{J(J+1)} \right]^2 \right\}^{1/2}, \quad (2)$$

where  $\Delta$  is the inversion splitting. The quadratic effect connected with the matrix elements  $\Delta J = \pm 1$  can be disregarded in the case of  $\text{NH}_3$ . Thus, for the ground state of  $\text{NH}_3$  we have  $\Delta_0 \approx 0.8 \text{ cm}^{-1}$ , for the excited state with  $v_2 = 1$  we have  $\Delta_2 \approx 35 \text{ cm}^{-1}$ , while at  $\mu E < \Delta/2$  the Stark energy of the ground state is much higher for the excited state with  $v_2 = 1$ . Therefore, it is possible to focus a beam of  $\text{NH}_3$  molecules in the ground state even in a field of 1 kV, whereas 50 kV and more is needed to focus a beam of excited  $\text{NH}_3$  molecules. In addition, ammonia absorbs  $\text{CO}_2$ -laser emission in the  $v_2$  band. Therefore, selection of excited states by the deflection method, or best of all by focusing with an inhomogeneous electric field, is feasible for ammonia.

We note in conclusion that the method in question can be used also for the selection of electron-excited states, since the dipole moment and the level structure of the molecules are as a rule greatly altered by electron excitation.

The author thanks V. S. Letokhov for active interest that has stimulated the present work, and to N. V. Karlov, S. S. Alimpiev, and B. G. Sartakov for a discussion of the results of [1] and of the present work.

<sup>1)</sup>The statements in [1] notwithstanding, the first term of (1) is not equal to the overtone transition moment, [1] and molecules having symmetry centers have no dipole moments [2-6].

An estimate of the second term of (1) for  $\text{CCl}_4$  in the two-atom approximations [7] yields 0.005 D for  $\text{CCl}_4$  [7] and 0.01 for  $\text{CH}_4$  [8]; the first and second terms of (1) are of the same order of magnitude. (The estimate  $\langle \mu_3 \rangle \sim 0.1 \text{ D}$  for  $\text{CCl}_4$  in [1] is patently too high. In addition, the conditions used in [1] for the linear Stark effect cannot be satisfied simultaneously, and there is no Stark effect [6,10] on the triplet. [1])

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