

Deflection of a beam of vibrationally excited molecules in an inhomogeneous electric field

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A method is proposed for selecting vibrationally excited molecules by deflecting a beam of the molecules in an inhomogeneous electric field. With a molecule of the ZY_4 type and T_d symmetry as an example, it is shown that vibrationally excited molecules acquire in a sufficiently strong electric field a constant dipole moment comparable in order of magnitude with the dipole moment of the vibrational transition. An estimate of the possible deflection angles is given.

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It is well known that the problem of isotope separation with a laser reduces to the problem of sorting out selectively excited particles having the required isotopic composition from the unexcited ones without loss of excitation selectivity. To separate the selectively excited particles from a molecular (atomic) beam, a method based on light pressure was proposed.^[1,2] In view of the small photon momentum, this method is not effective enough. In this paper we analyze the possibility of selecting vibrationally-excited molecules in a strong inhomogeneous electrostatic field.

It is known that sorting of molecules by energy states of the inversion spectrum in an inhomogeneous electric field was used to develop the maser based on a beam of ammonia molecules.^[3] The separation mechanism in this case was in essence the quadratic Stark effect,^[4] the energy of the interaction of the molecule with the field being of the order of $(\mu E)^2/\hbar\omega$, where E is the intensity of the static field, μ is the dipole moment, and $\hbar\omega$ is the quantum of the inversion transition. In the radio band ($\omega \sim 2\pi \cdot 10^{10} \text{ sec}^{-1}$), this energy is quite high. On going to vibrational spectra of the molecules ($\omega \sim 2\pi \cdot 10^{13} \text{ sec}^{-1}$), the quadratic Stark effect does not provide a sufficient degree of separation at reasonable values of the field intensity E .

At the same time, symmetrical molecules that have no dipole moment in the ground vibrational state acquire, as follows from the estimates presented below, a constant dipole moment that coincides with the dipole moment of the second-harmonic vibrational transition when degenerate oscillations are excited in the presence of a sufficiently strong electrostatic field. The vibrationally-excited molecules are then deflected by the inhomogeneous electric field within the framework of the linear Stark effect.

By way of example we consider molecules of the type XY_4 and symmetry T_d . Such a molecule has one A_1 vibration mode (ν_1), one E mode (ν_2), and two F_2 modes (ν_3 and ν_4). We assume that the energy of the interaction of the field with the molecule is much larger than the energy of the Coriolis interaction $2B\xi J$, where B is the rotational constant, ξ is the Coriolis constant, and J is the rotational quantum number. For the CCl_4 molecule, according to the data of^[5], it suffices to use a field $E \gg 10 \text{ cgs esu}$. Neglecting the Coriolis interaction, the levels of the ν_3 oscillations are triply degenerate. We

assume also that the energy of the interaction of the field with the molecule is smaller than the distance between the vibrational sublevels $2BJ$, so that we can seek the ψ function of the molecule in the form

$$\psi_{\text{mol}} = \psi^{el} \psi^r \sum_i C_i \psi^v_i \quad (1)$$

where ψ^{el} , ψ^r , and ψ^v are respectively the electronic, rotational, and vibrational ψ functions. The problem of finding the energy of the interaction of the molecule with the field then reduces to diagonalization of the vibrational Hamiltonian of a molecule situated in a field, followed by separation of that part of the energy which is linear in E .

The Hamiltonian in question is of the form

$$\hat{H} = \hat{H}_0 - \hat{\mu} E \quad (2)$$

where \hat{H}_0 is the vibrational Hamiltonian of the molecule outside the field E . The molecule dipole-moment operator $\hat{\mu}$ is represented in the form

$$\hat{\mu} = \hat{\mu}_0 + \left(\frac{\partial \hat{\mu}}{\partial Q_i} \right)_0 Q_i + \frac{1}{2} \left(\frac{\partial^2 \hat{\mu}}{\partial Q_i \partial Q_j} \right)_0 Q_i Q_j \quad (3)$$

where Q_i and j are the normal coordinates of the vibrations. Here μ_0 is the constant dipole moment and is equal to zero for symmetrical molecules in the ground state, while $(\partial \hat{\mu} / \partial Q_i)_0 Q_i$ and $(\partial^2 \hat{\mu} / \partial Q_i \partial Q_j)_0 Q_i Q_j$ have respectively the meaning of the matrix elements of the vibrational transitions $0 \rightarrow 1(\mu_{01})$ and $0 \rightarrow 2(\mu_{02})$. The third term in the expansion (3) is due to the so-called electro-optical anharmonicity.

Writing down the vibrational Hamiltonian with allowance for the symmetry of the molecule, accurate to terms proportional to the third power of the normal coordinates of the vibrations ν_3 and ν_4 , and rewriting the obtained expression by means of a change of variable in the form typical of the Hamiltonian of a molecule not situated in an electric field, we obtain an expression for a certain effective constant dipole moment of the molecule

$$d = \frac{1}{2} [\mu_{02} + a\mu_{01}] \quad (4)$$

where a is the dimensionless constant of the cubic anharmonicity. In order of magnitude we have $a \approx \sqrt{\Delta\omega/\omega} \approx 0.1$, where $\Delta\omega$ is the frequency shift due to the mechanical anharmonicity. The quantities μ_{01} and μ_{02}

are connected by the relation $\mu_{02}/\mu_{01} \approx \sqrt{\alpha_{02}/2\alpha_{01}}$, where α_{01} and α_{02} are the absorption coefficients in the transitions $0 \rightarrow 1$ and $0 \rightarrow 2$. For molecules of the XY_4 type, the $0 \rightarrow 2$ transition is sufficiently well allowed and it can be assumed that $\mu_{02} \approx 0.1 \mu_{01}$.

As seen from (4), for molecules of this class the value of d for the allowed transitions can amount to several tenths of a Debye.

The angle of deflection of a molecule beam having a moment d in a field with gradient ∇E and length l is

$$\beta = \frac{d\nabla E l}{M_0 V^2} \frac{MK}{J(J+1)}, \quad (5)$$

where M_0 is the molecule mass, V is the velocity, and J , M , and K are the rotational quantum numbers. At $M_0 = 2 \times 10^{-22}$ g, $V = 2 \times 10^4$ cm/sec, $M = K = J$, $d = 0.1$ D, $l = 20$ cm, and $E = 10^4$ cgs esu^[6] we have $\beta \approx 15^\circ$.

Analogous effects can appear for molecules belonging to other types of symmetry, but having no inversion

center. In molecules with O_h symmetry (XY_6), the presence of an inversion center, generally speaking, hinders the appearance of the considered effect. Nonetheless, the violation of the symmetry upon excitation of the oscillations seems to lead to the appearance of an effective dipole moment. The breakdown of the O_h symmetry of molecules of type XY_6 is apparently evidence of the experimentally observed^[7] lifting of K degeneracy.

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