Influence of internal molecular degrees of freedom on their electric and optical properties

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Electric properties of molecules, such as dipole moment and dipole polarizability, determine the variety of optical and electrical phenomena in molecular gases and play a dominant role in intermolecular and electron-molecular interactions [1].

It is known that excitation of internal degrees of freedom of molecules can significantly affect their electrical properties [2], which can lead to a change in the refractive index of a molecular gas, and affect the transport properties and the rates of chemical reactions.

The dependences of the electric dipole moment and static polarizability for a number of diatomic molecules important for combustion chemistry and the atmosphere (H2, N2, O2, NO, OH, CO, CH, HF, and HCl) were calculated for a wide range of internuclear distances on the base of quantum chemistry methods. The effective values of the dipole moment and the static polarizability of molecules in individual vibrational and rotational states were obtained up to the dissociation limit. It is shown that the excitation of the vibrational states of diatomic molecules can significantly (up to 1.5-3 times) affect the effective values of the dipole moment and the static polarizability averaged over the vibrations, while the effect of excitation of rotational states is weaker pronounced.

For a wide range of polyatomic molecules and atomic clusters (50 structures) that are of interest for a number of practical applications (materials science, combustion chemistry, atmospheric chemistry), the state-specific values of the dipole moment and polarizability were calculated. It is shown that the character of the influence of vibrational excitation on the electrical properties of polyatomic molecules is significantly different for individual vibrational modes.

For the molecules and clusters under consideration, an analysis of the effect of excitation of vibrational degrees of freedom on electric properties with respect to such properties as the refractive index and the diffusion coefficients was conducted.

Special attention was paid to the determination of the electrical properties of electronically excited molecular oxygen in the singlet $a1\Delta g$ and $b1\Sigma g+$ states owing to their importance in the atmospheric, combustion, and electric discharge chemistry.

This work was supported by the Russian Foundation for Basic Research (project No. 17-01-00810).

References

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