Electric Field Dependence of the Ionization Threshold of Benzene and the Benzene-Argon Complex

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Z. Naturforsch. **36a**, 1257—1258 (1981);
received October 14, 1981

The ionization potential measured as a threshold to photoionization for benzene and the benzene-argon complex is shown to be a strong function of the applied electric field required to detect the ionization event. The ionization potential is lowered by moderate electric fields and the field dependence is found to be the same for the bare molecule and its Van der Waals complex. The data can be fitted with a square root dependence on the electric field and this shows that large molecules behave like atoms at the ionization threshold.

Ionization of large molecules can readily be performed with lasers by way of resonant two photon ionization [1]. The position of the threshold and the behaviour near to it can be studied by scanning the energy of the second photon. Due to the narrow bandwidth of the lasers used extremely accurate values of the ionization potential can be obtained [2]. The high resolution of this technique reveals a dependence of the measured ionization potential on the draw-out electric field.

To eliminate the influence of sequence congestion at room temperatures, caused by the high number of degrees of freedom in large molecules, the measurements have to be performed in a hypersonic jet. Thus pure rovibronic levels can be excited [3] from which the ionization can occur. In the hypersonic jet the molecules are seeded in noble gases; at higher pressures of the driving gas molecular complexes are produced [4]. These Van der Waals complexes can similarly be ionized via resonant two colour photoionization, which has been shown to produce stable complex ions [2]. It is also possible to study the ionization potential at the threshold of these weakly bound complexes.

In our experiment benzene is seeded in argon and the ionization is achieved with two dye lasers pumped simultaneously from one Nd: YAG laser [2]. The first photon populates the resonant state (ν_6 of the S_1 state) and the absorption of the second photon leads to ionization. The ions are extracted from the jet by an electric field which can be adjusted up to 400 Volts/cm. The detection of the ions is performed with a time of flight mass spectrometer, which also permits to separate contributions from the bare molecules and their complexes.

When we changed the electric field from 60 Volts/cm to 360 Volts/cm an interesting effect occurred. The ionization threshold also changed showing a strong red shift with higher electric fields [5]. The shift is not linear with the electric field but follows roughly a square root dependence. The experimental results for benzene are shown in Figure 1a. At a field of only 370 Volts/cm a shift of 120 cm^{-1} corresponding to 14.9 meVolt is observed. The same measurement was performed for the benzene-argon complex. As the signal from the complexes is much lower than that from the bare benzene molecule, and it also diminishes at lower extraction fields,

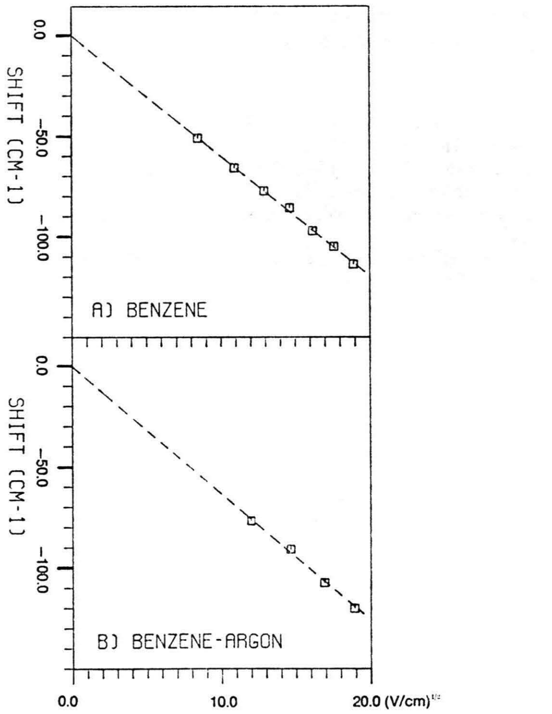

Fig. 1. a) Electric field dependence of the ionization threshold for benzene □ experimental values, --- least squares fit for a square root dependence. b) Electric field dependence of the ionization threshold for the benzene-Argon complex □ experimental values, --- least squares fit for a square root dependence.

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only the threshold at four different field strengths could be obtained. The results are shown in Figure 1b.

If one assumes in the simplest model that the Coulomb potential for a Rydberg electron is superimposed with a linear potential of a field strength E, the lowering of the threshold should be proportional to the square root of the applied electric field [6]. Our experiment leads to a red shift of $5.97\sqrt{E}\ \mathrm{cm}^{-1}$ for E in Volts/cm. This means that a field of typically 50 Volts/cm produces an error of 43 cm^{-1} in the ionization potential measured, a value well within the range of high resolution methods.

Atomic sodium shows a similar effect in which the critical ionization field for a given Rydberg state follows this square root dependence, but the critical field is always larger than the one given by the simple model [7], which is explained as a Stark shift on the ionization.

In our case, the electric field which is necessary to shift the threshold by a certain amount is also larger than the one predicted by this model but it is nearly the same for benzene and the benzene argon complex.

The threshold behaviour is not a sharp step function but shows a width of about 30 cm^{-1}, which is much broader than the resolution of about 0.5 cm^{-1} of the laser system. The width is slightly decreasing for lower electric fields, and is also indicating a Stark field effect in the ionization process.

From these measurements one can see that the large molecules and their Van der Waals complexes behave like atoms in their field dependence of the ionization threshold; the difference in the size appears to be of no importance. The complexation with argon reduces the ionization threshold but does not affect the behaviour at the threshold. Accurate modern measurements of ionization potentials almost invariably measure the onset of a current produced by a draw-out field. These measurements will be in error if this field dependence is not considered.

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