

Short communication

Long-lived negative ion formation by Alq₃

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Abstract

Organic electroactive molecule Alq₃ has been investigated by means of Electron Capture Negative Ion Mass Spectrometry (ECNI MS). Only extremely long-lived parent molecular NIs were detected in the electron energy region 0–1 eV. Mean lifetime τ_a of these ions decreases from $\sim 800 \mu\text{s}$ at $\sim 0 \text{ eV}$ to $400 \mu\text{s}$ at 0.8 eV . The results of τ_a measurement allow to estimate adiabatic electron affinity $1 < EA_a < 3 \text{ eV}$ in the framework of the model of autodetachment elaborated by Christophorou and co-workers.

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1. Introduction

A large number of organic electroactive compounds suitable for thin film applications in optoelectronics [1] have been developed up to date. It is known that electron-accepting molecules can make much easier electron tunneling from the metal cathode in electric field. Thin films made from such materials are supposed to have electronic type of conductivity. As a rule, electron transporting materials can form long-lived negative ions due to nondissociative attachment of an additional electron to neutral molecule. Tris(8-hydroxyquinolino)aluminum (Alq₃) is a classical electroactive molecule widely applied in organic electroluminescent devices [1–3]. Therefore, investigation of its electronic structure, in particular interactions with free low-energy electrons, is actual. Collisions of electrons with energies up to 50 eV with Alq₃ revealed transitions into singlet and triplet states [4]. A small evidence of NI formation is appeared in electron energy loss spectra [4] near elastic scattering peak, i.e., at thermal and near thermal energies. On the other hand, Electron Capture Negative Ion Mass Spectrometry (ECNI MS) is a powerful tool for investigation of electron structure of negative ions [5]. Long-lived molecular NI formation is known since sixties

[6]. Christophorou et al. developed the theory of autodetachment and verified it at numerous number of lifetime (τ_a) measurements [7–9]. Measurements of τ_a may be used for preliminary estimation of the value of electron affinity (EA) of the target molecules in the framework of this model [8]. Nevertheless, only few works were devoted to long-lived molecular NI investigations and autodetachment lifetime measurements last decade [10–13].

2. Experiment

ECNI mass spectrum of Alq₃ was measured using a modified [5] MI-1201 mass spectrometer under the following conditions: accelerating voltage 4 kV, electron trap current $\sim 1 \mu\text{A}$, FWHM of electron energy distribution $\Delta E_{1/2} = 0.4 \text{ eV}$, energy of electrons E_{el} varies in the range of 0–12 eV. This type of instrument allows to measure NI curves of effective yield (CEY) as a function of electron energy. Focusing magnet for the electron beam collimating is not shown in Fig. 1. Typical ion source potentials were the following: potential of the anode chamber (#1 in Fig. 1), defined the energy of the electron beam, is varied in the range $-1 < U_{el} < +13 \text{ V}$; the first and the second electron focusing lens (#4) $-1 < U_{1ef} < 0 \text{ V}$, and $0 < U_{2ef} < +2 \text{ V}$, respectively; the repel potential (#7) $-0.8 < U_r < -0.2 \text{ V}$; the ion extraction and the ion focusing lens potentials (#10) $U_{ext} \sim 10 \pm 10 \text{ V}$, and $U_{if} \sim \pm 50 \text{ V}$, respectively. All tuning potentials are

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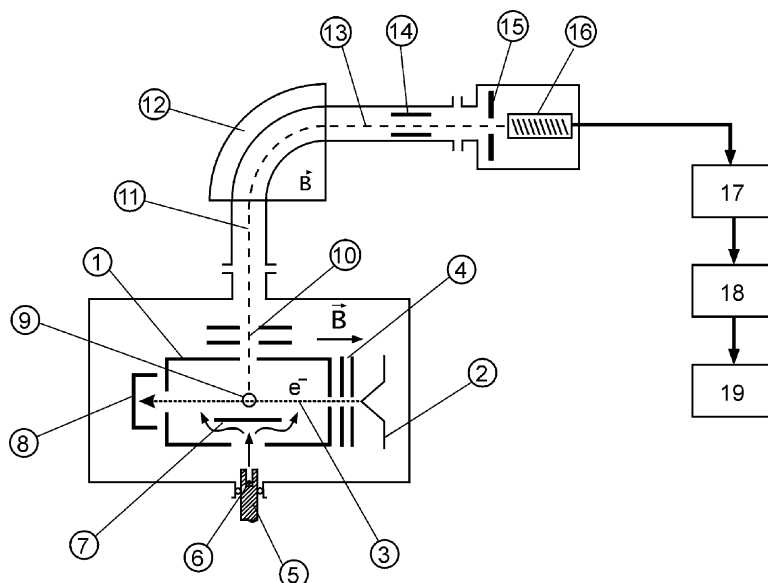


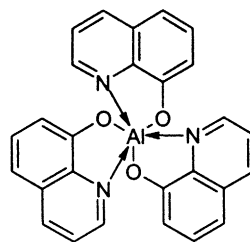
Fig. 1. Schematic view of the ECNI mass spectrometer. Notations: 1, heating reaction chamber (anode chamber, stainless steel, $T = 80\text{--}300^\circ\text{C}$); 2, tungsten filament; 3, electron beam; 4, electron optics; 5, heating inflow system (stainless steel rod); 6, sample under investigation (evaporating); 7, repel electrode; 8, electron collector; 9, interaction region; 10, ion extraction and focusing lens; 11, first free-drift region; 12, magnet analyzer; 13, second free-drift region; 14, deflection plates; 15, ion optics; 16, secondary electron multiplier; 17, pulse multiplier; 18, detection system; 19, control and record system.

varied in the wide range for the proper adjustment of the ion source. It is possible to measure mean autodetachment lifetime τ_a of NI according to the method developed by Khvostenko et al. [5] for static magnet mass spectrometer measurements. Deflection plates (#14 in Fig. 1) allow to deviate charged species from the multiplier entrance and to measure the neutrals' signal only. When there is no deflecting voltage on the plates #14, then the multiplier detects total particle (ion + neutrals) current $I_p = k_1 N^- + k_2 N^0$; otherwise, when deflection voltage is switched on ($U_d \sim 1\text{ kV}$), then the neutrals, formed in the second free-drift region (#13 in Fig. 1), are detected only, $I_0 = k_2 N^0$; k_1 and k_2 are the amplification factors for the ions X^- and neutrals X^0 of X , respectively; N^- and N^0 are the number of IN and neutrals. τ_a may be calculated according to appropriate formula [5]:

$$\tau_a(X^-) = \frac{t(\text{SF}_6^-)}{\ln[1 + (k_1 I_0 / k_2 (I_p - I_0))]} \sqrt{\frac{M_X}{M_{\text{SF}_6^-}}}, \quad (1)$$

where $t(\text{SF}_6^-) = 5.95\ \mu\text{s}$ is the time-of-flight of SF_6^- in the second free-drift region; M_X is the molecular mass of X ; $M_{\text{SF}_6^-} = 146\text{ amu}$. Amplification factors were $k_1 = 8 \times 10^5$ and $k_2 = 4.74 \times 10^5$ in our measurements. At the first step we measure $\text{SF}_6^-/\text{SF}_6$ lifetime with the aim to find k_1/k_2 ratio from Eq. (1). It is assumed that autodetachment lifetime of $\text{SF}_6^-/\text{SF}_6$ $\tau_a = 68\ \mu\text{s}$ [14]. At the second step, we measure the particle and neutral current of the ion under investigation, and calculate $\tau_a(X^-)$ using formula (1) in supposition that the ratio $k_1/k_2 = \text{constant}$ for the different masses. Time-window of τ_a measurements is about 5–5000 μs .

Alq_3 was synthesized and purified by manifold sublimation. The chemical structure of Alq_3 is presented below:



Despite Alq_3 is a chelate molecule, it is rather stable. The temperature of thermal decomposition threshold is about 310°C . Vaporization of Alq_3 was reached at the temperature $\sim 150^\circ\text{C}$ of the rod. The temperature of the ion source was kept $\sim 80^\circ\text{C}$. Molecules under investigation multiple collide with the ion source walls before ionization event due to special construction of the ion source. Therefore, the internal vibration energy of the target molecules corresponds to the temperature of the ion source.

3. Results and discussion

The results obtained are presented in Fig. 2. Only long-lived molecular NI (main isotope m/z 459 amu) are detected in the NI spectrum of Alq_3 . The shape of the Alq_3^- CEY shows clearly that there are more than one long-lived resonant states in the energy region 0–0.9 eV. Really, the full weight of Alq_3^- CEY in the half-maximum FWHM $> 0.6\text{ eV}$, and $\text{FWHM}(\text{SF}_6^-) \sim 0.4\text{--}0.45\text{ eV}$ (see Fig. 2). It is obvious that the anion, living some thousand microseconds, exists in the ground electron state, independently from its initial electron state and primary mechanism of its forma-

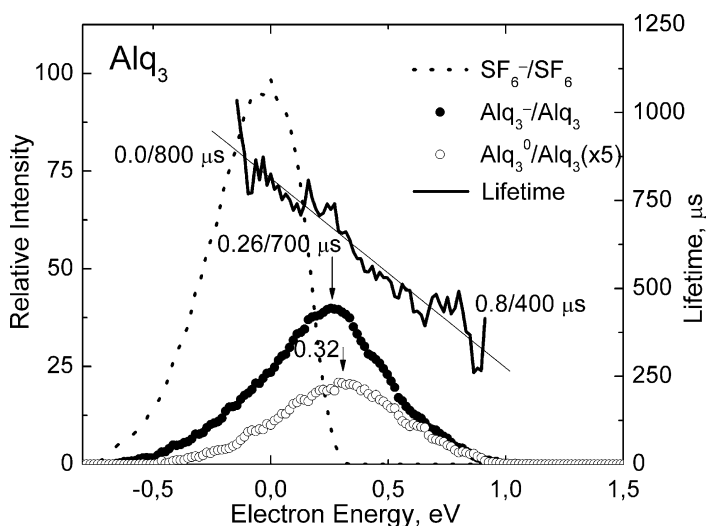


Fig. 2. Curves of effective yield SF_6^-/SF_6 , Alq_3^-/Alq_3 , and Alq_3^0/Alq_3 , left axes, together with mean autodetachment lifetime (right axes) as a function of electron energy. Marks show lifetime energy dependence.

tion, either the nuclear excited Feshbach resonance or the shape resonance. Mean lifetime of molecular NI, relative autodetachment, practically linearly decreases with the electron energy. Such kind of the energy dependence of τ_a is very strange because of typical behavior of τ_a as a function of the incident electron energy should be exponential [7,8]. It is known that the calculated τ_a function always decreases much faster with the energy than experimental one. This effect has been explained by Christophorou [9] and is attributed to the poor electron energy resolution in the experiment ($\Delta E_{1/2} \sim 0.45$ eV in our measurements). Possible, this effect may lead to distortion of the observed $\tau_a(\varepsilon)$ shape right up to the linear dependence. So, measured linear decrease of the autodetachment lifetime is an artifact of the low-energy resolution [9].

4. EA estimation

Measured decreasing of τ_a with the energy, in principle, may be considered in the framework of a statistical model elaborated by Christophorou et al. [8]. However, this theoretical approach requires knowledge of the dominant parameter of the model, the EA of the target molecule. Unfortunately, up to now there are no available data on EA of Alq_3 . So, only qualitative consideration of Alq_3^- formation and autodetachment decay is possible. On the other hand, as it has been pointed out previously [7], the value of EA may be evaluated by this model if we accept certain initial assumptions. Therefore, let us try to solve the inverse problem of EA estimation by known lifetime energy dependence.

Generally speaking, Christophorou's model has two basic parameters which define the value of autodetachment lifetime: EA and number of effective degrees of freedom N' participating in the sharing of the ion's excess energy [8].

The main equation is as following:

$$\tau^{-1} = \frac{\sigma(\varepsilon_i)\varepsilon_i^{1/2}}{[\varepsilon_i + EA + a\varepsilon_z]^{N-1}} \left[\frac{m}{\pi^2\hbar^3} (\varepsilon_i + a'\varepsilon_z)^{N+1/2} I \right], \quad (2)$$

where $\sigma(\varepsilon_i)$ is the electron capture cross-section, ε_i is the initial electron energy, m is the electron mass, ε_z is the zero-point energy of the molecule, a and a' are known correction factors, $N = 3n - 6$ is the number of vibrational degrees of freedom.

For the sake of the main case of Alq_3 , $N = 150$, $\sigma_C(\varepsilon_i)$ may be fitted by Gaussian function:

$$\sigma_C = \frac{A\sqrt{2}e^{(2(\varepsilon-\varepsilon_C)^2/w^2)}}{w\sqrt{\pi}}, \quad (3)$$

with the following parameters: $A = 83.6$, $\varepsilon_C = 0.26$, $w = 0.7$. Other necessary parameters are the following: $a = 0.85$; $a' = 1.0$; $EA = 1$ eV; $\sigma_C(\varepsilon_C) = 95 \text{ \AA}^2$. The last value has been estimated from quantum chemical calculations of the optimal geometry of the neutral molecule. This is the parameter set #1. The value of EA was chosen for the best fit with the experimental value of autodetachment lifetime. The results of estimation of the autodetachment lifetime are presented in Fig. 3. Comparison of the experimental measurements of τ_a (Fig. 2) and its theoretical evaluations (Fig. 3) shows reasonable agreement at the peak maximum $\varepsilon_i = 0.26$ eV. The calculated function decreases much faster with the energy than experimental one, the same as in the case of the original theory [7,8]. This effect has been explained by Christophorou [9], and is attributed to the poor electron energy resolution in the experiment ($\Delta E_{1/2} \sim 0.4-0.45$ eV in our measurements). So, if our parameter set #1 for calculation of τ_a is reasonable enough, then the adiabatic EA of Alq_3 is about 1 eV. It is necessary to point out that such kind

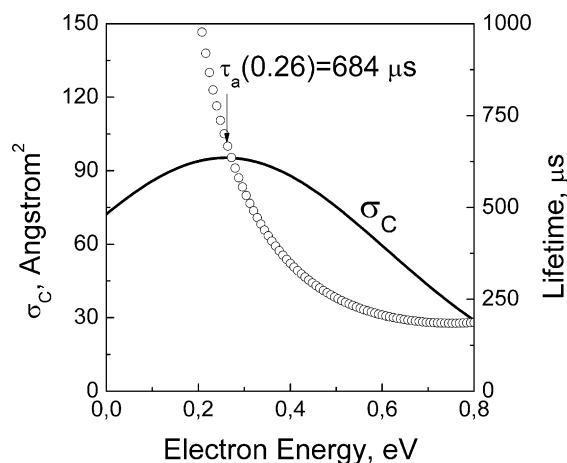


Fig. 3. Calculated autodetachment lifetime as a function of electron energy (circles) together with Gaussian fitted electron capture cross-section (line). Parameter set #1, see text.

of autodetachment lifetime evaluation is very approximate. Nevertheless, unknown values of the parameters a and a' , which influence on the effective number of degrees of freedom in the target molecule and anion, make our evaluations ambiguous. Really, if $a = a' = 1$, parameter set #2, and all the other parameters are the same in set #1, then the value of EA should be ~ 3 eV. So, lifetime measurement may be used for preliminary estimation of the Alq_3^- EA.

The shape of Alq_3^- curve of effective yield indicates that vertical EA = -0.26 eV, according to the Alq_3^- peak maximum. In accordance to generally accepted classification [15], this is a shape resonance which relaxes into the ground electronic state of the anion, as it has been proposed by Cooper et al. [16] for the case of *p*-benzoquinone. Theoretical estimations, according to Ref. [8], predict adiabatic EA in the range from 1 to 3 eV, depending of the effective number of degrees of freedom sharing the ion's excess energy.

5. Conclusion

Curve of effective yield of Alq_3^- shows that the vertical EA = -0.26 eV for this molecule. Obvious, measured linear decrease of the autodetachment lifetime is an artifact

of the low-energy resolution [9]. Autodetachment molecular NI lifetime measurements, $\tau_a = 700 \mu\text{s}$ at 0.26 eV, allows to estimate, as a preliminary, the adiabatic EA of the target molecule as 1–3 eV in the framework of the autodetachment model proposed by Christophorou et al. [7,8].

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